NEWER METHODS
OF
VOLUMETRIC CHEMICAL ANALYSIS

By

Erna Brennecke, *Fresenius Chemical Laboratory,* Wiesbaden; N. Howell Furman, *Princeton University;* Hellmuth Stamm, *University of Halle;* Rudolf Lang, *Technical School,* Brünn; and Kasimir Fajans, *University of Michigan*

WILHELM BÖTTGER
Editor

Translated by
RALPH E. OESPER
Associate Professor of Analytical Chemistry,
University of Cincinnati

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PREFACE TO THE AMERICAN EDITION

In chemistry, as in other branches of science that are undergoing rapid growth, there is a marked lag in the penetration of new developments into circles which perhaps might profit most from the assimilation of this fresh material. The analytical chemists are not exceptional in this regard and the reasons for their failure to take advantage of the newer knowledge are not hard to find. The more recent, and possibly better, procedures are not adopted because the analyst who is actively practicing his profession intuitively relies on what he was taught as a student. Furthermore, the industrial laboratory is commonly confronted with a host of problems whose satisfactory solution is expected within a minimum of time. This leaves the analytical chemist little chance to follow the current literature of his specialty, and he has still less opportunity to test the methods and check the frequently conflicting statements in what he does read.

These circumstances prompted the editor of the series *"Die chemische Analyse"* to arrange for the compilation of a volume on *"The Newer Methods of Volumetric Analysis."* This branch of quantitative chemistry is especially important, particularly in industrial laboratories where speed is a factor of prime importance. In addition, remarkable progress has been made in this field during the past two decades.

The success of this plan was primarily dependent on the editor's ability to find collaborators who either had laid the foundations of new general methods and who consequently could treat the particular topic with competence and authority, or who, because of their extended and intensive acquaintance with the recent proposals, had become expert in the extension of the general methods to definite individual cases.

The editor's good fortune in the selection of his co-workers was evidenced by the favor accorded to the first (1935) edition, which was quickly sold out. Instead of reprinting, it was decided to prepare a revised, enlarged text. In this some of the discussions were recast, the literature references were brought down to date and an entire new chapter, on alkaline permanganate, was added. This second edition forms the basis of the translation presented here.

The symposium now contains seven discussions: (I) The Elimination of the Titration Error in acidimetric and alkalimetric titrations, by E.

Brennecke; (II) Ceric Sulfate as volumetric oxidizing agent, by N. H. Furman; (III) Alkaline Permanganate solution as volumetric oxidizing agent, by H. Stamm; (IV) Iodate and Bromate methods, including Manchot's bromometric procedure, by R. Lang; (V) Chromous solutions as volumetric reducing agent, by E. Brennecke; (VI) Oxidation-Reduction Indicators, by E. Brennecke; (VII) Adsorption Indicators for precipitation titrations, by K. Fajans.

These topics have been treated with two objectives in mind: (a) exposition of the theory underlying the new method, so that an insight may be gained into the reasons for the way in which the subject has been developed, and (b) the presentation, so far as possible, of an exact set of directions for the performance of particular analyses.

The writers and the editor have endeavored to make the treatment uniform. Some of the topics lend themselves to a stronger emphasis on the theoretical aspects and the possibilities of future development, as opposed to others in which the greater stress is on the existing satisfactory procedures. The chapter contributed by Professor Fajans is somewhat different than the others. It is built up mainly on hitherto unpublished studies and their theoretical implications, while the results and procedures accessible in the literature are given in a much briefer, summarized form.

To make it easier for the practicing chemist to acquire detailed information as to the numerous applications of the new methods and the experience that has been gained from these trials, each chapter is supplemented with a carefully selected bibliography. The length of these comprehensive lists demonstrates in unmistakable fashion the extent to which these newer methods have already become a part of the professional equipment of progressive analytical chemists.

The successful completion of this book is due almost entirely to the self-sacrificing cooperation of the authors. They accepted willingly the suggestions of the editor, and, in turn, contributed meritorious comments and proposals. The editor gladly acknowledges his debt to all of them.

The issue of an American edition is a source of great satisfaction to the editor because the chemists of the New World have made important and notable additions to the progress of the theory and practice of modern analytical chemistry. In conclusion, he wishes to thank his friend, Professor Ralph E. Oesper, for consenting to prepare the translation.

WILHELM BÖTTGER

Leipsic, January, 1937

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PART I

ELIMINATION OF THE TITRATION ERROR IN ACIDIMETRIC AND ALKALIMETRIC TITRATIONS

BY

ERNA BRENNECKE

ELIMINATION OF THE TITRATION ERROR IN ACIDIMETRIC AND ALKALIMETRIC TITRATIONS

For the past several decades acidimetric indicators have been the subject of much study, not merely from the standpoint of their application in volumetric analysis but also with respect to their use in colorimetric pH determinations. The fundamental ideas underlying the applicability of these indicators for titrations were set forth in considerable detail as early as 1914 by Bjerrum in his well known monograph.[1]

An acquaintance with the facts of acidimetric titrations sufficient for all practical purposes may therefore be assumed. The following discussion, where use will be made of the findings of the newer methods of investigating this problem, will serve then only to elucidate the viewpoints essential to the evaluation of the indicator error. With this as a basis, there will then be given a procedure which easily permits the operator to exclude, to a considerable extent, the various sources of error, and thereby reach results of greater accuracy.

GENERAL CONSIDERATIONS OF THE BEHAVIOR OF ACIDIMETRIC INDICATORS

The Transition Range. Acidimetric indicators are characterized by the well known fact that the formation of their salts goes hand in hand with a change in constitution, which in turn results in an intensive color change. The salt formation will occur at higher or lower hydrogen ion concentrations, depending on the dissociation constant of the (moderately strong or weak) acid or base that is being used as indicator. It follows then, that every indicator has a very definite *transition range* in which the two colored forms go over into one another. By means of the mass law, it can be shown, for example, that for a monobasic indicator acid[2] the hydrogen ion concentration and the concentrations of the two differently colored forms of the indicator are related:

$$\frac{[I^-]}{[HI]} = \frac{K_{Ind}}{[H^+]}$$

---

[1] Bjerrum (74), in the Bibliography at the end of this Part; see also Kolthoff (76, 77).

[2] Indicator bases may be considered in exactly the same way. The dissociation relations of amino-azo indicators are discussed by Küster (1), Bjerrum (2), Kolthoff (3).

From this expression it follows that for a 50 per cent transformation of the indicator there corresponds a hydrogen ion concentration numerically equal to the (apparent)[3] dissociation constant of the indicator. Bjerrum proposed that the hydrogen ion exponent corresponding to this concentration be called the *indicator exponent*, p_I. Thiel calls it the mid-point, $p_{H\frac{1}{2}}$. It is the fundamental characteristic of an indicator.

The eye has only a limited ability to detect color changes and, in general, this limitation is such that less than 10% of the one form cannot be perceived in the presence of the other. Consequently the pH values within the transition range of the indicator are given by the relation:

$$p_I - 1 < pH < p_I + 1$$

For this reason, transition ranges of indicators extend over about two pH units, a figure repeatedly confirmed by experiment.

Table I demonstrates an important fact, namely, that quite different amounts of acid are required to bring about a change in pH of two units.

TABLE I

Change of pH	cc. 0.1 N HCl[4] per 100 cc. final volume
7–5	0.01
5–4	0.09
4–3	0.9
3–1	99

These figures illustrate three experimental facts:

(1) An indictor whose transition lies at high pH values will show a distinct color change on the addition of much smaller quantities of acid (and also on the addition of weaker acids, CO_2, for example) than an indicator which changes only in a more strongly acid range and which consequently does not respond to slight changes in hydrogen ion concentra-

---

[3] It is necessary to speak of an "apparent" constant because it includes the equilibrium between the true indicator acid and the ψ acid produced by the change in constitution.

[4] The volume of 0.1 N acid or base required to reach a particular pH value may be easily calculated with the aid of the Bjerrum expression for the H^+ (or OH^-) error: $e_H^+ = c_H^+ \cdot \frac{v}{n}$. Here c_H^+ = concentration of the hydrogen ion at the end of the titration, v = total volume of the solution, n = normality of the standard solution. The dependence of the indicator error on v and n is clearly brought out in this formula.

tion. Correspondingly, an indicator with an indicator exponent of about 10 will not respond to weak bases, because they can produce only inconsiderable changes in the high hydroxyl ion content of the solution.

(2) With indicators whose transition interval spans lower pH values, the solution to be titrated and the solution in the burette may not be too dilute, otherwise a drop of the titrant will not cause a visible change. The corresponding requirements hold for indicators with extremely high p_I.[5]

(3) With methyl yellow, for example, which has a transition interval of pH 2.9–4.0, it is by no means immaterial, with a decinormal titrant, whether the change is from yellow to red, or from red to yellow.

A further fact to be kept in mind when using indicators is the *variability of the transition interval and indicator exponent* with composition and temperature of the solution, and with the thickness of the layer under observation. As to the composition of the solution, not only the indicator concentration must be considered, but also very particularly, any content of neutral salt or alcohol.[6]

The Indicator Concentration. *The influence of the indicator concentration* is most evident with *one color indicators* because with them it is only the concentration of the colored form which determines the beginning of the perceptible change. For example, depending on the concentration, the first pink with phenolphthalein may appear at a pH between 8.2 and 9.2.[7]

With *two color indicators* the influence of the concentration on the change is dependent on several factors (relative color intensities, solubility of the two indicator forms, etc.) and consequently the variation is much greater from case to case.[8]

The Neutral Salt Effect. On the basis of the theory of strong electrolytes, the neutral salt effect may be accounted for by the following transformation of the mass law expression mentioned before:[9]

$$\frac{a_{I^-}}{a_{HI}} = \frac{K_a}{a_{H^+}} \text{ or } \frac{[I^-]f_{I^-}}{[HI]f_{HI}} = \frac{K_a}{[\mathrm{H}^+]f_{\mathrm{H}^+}}$$

---

[5] In this connection, see Kolthoff (4).

[6] It is well known that sense perception and the purity of the indicator play a rôle in the recognition of a definite color.

[7] Kolthoff (76), Vol. 2, p. 67.

[8] Kolthoff (77), p. 193. See Bjerrum [(74), p. 88] for more exact statements concerning the small quantities of acid or base consumed by the indicator.

[9] See e.g. Brönsted (5), Thiel and Coch (6), and especially Falkenhagen (78).

That is, for the equilibrium between the reactants it is not their concentrations which are decisive, but the *activities* (a) which alone are thermodynamically effective. These activities may be obtained from the concentrations by multiplying them by the corresponding *activity coefficients* (f). In solutions containing little electrolyte the activity coefficients are practically equal to unity, and the expression just given then becomes the simple mass action equation. The ions if present in greater concentration bring about, through the electric fields which they produce, primarily a decrease of the activity coefficients of the indicator ions (more generally, of the ions of the electrolyte) and to a small extent an increase in the activity coefficient of the undissociated molecule (f_{HI}). The essential difference between the activities and the concentrations lies, therefore, in the fact that in the former, account is taken of the influence of all the electrolytes present in the solution upon the molecule or ion under consideration.[10]

The neutral salt effect or the electrolyte effect reveals itself in the case of indicators, as it does with all weak electrolytes, primarily by a *rise in the dissociation.* Since the *color shade* is determined above all by the *concentration ratio,* that is $\frac{[I^-]}{[HI]}$, the addition of a salt would, in the case of an acid indicator, favor the form stable at the higher pH; on the other hand, the form stable at the lower pH will be favored with basic indicators.

The application of the foregoing equation is simplified by the fact that the activity of the H^+ ions is obtained directly by potential measurements with the hydrogen electrode. The equation then can be rewritten:[11]

$$\log \frac{f_{I^-}}{f_{HI}} = \log K_a + P_H + \log \frac{[HI]}{[I^-]}$$

The salts, however, may affect indicators in still another way. v. Halban and Ebert[12] found that, in the case of nitrate and picrate solutions, the extinction curves of the absorbing ions could be quantitatively and qualitatively altered. Thiel and Coch (6)[13] thereupon studied various acidimetric indicators with respect to their extinction and also observed a greater or less marked change of the colors of the two indicator forms according to the electrolytes present in the solution.

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[10] The activity coefficients can be found from determinations of solubility, measurements of the potential, or freezing point depression.

[11] See Brönsted (5). Concerning the activity coefficients of several indicators, see, for instance, Sendroy and Hastings (7).

[12] See also v. Halban, and Eisenbrand (9).

[13] Compare also the observation of v. Szyszkowski (10), and p. 15.

Furthermore, the possible precipitation of the indicator in the presence of larger salt concentrations should be kept in mind.[14] Among the indicators most commonly used, methyl yellow requires particular attention in this respect (4).

The Effect of Alcohol. The addition of *alcohol* may change the equilibrium relationships in an electrolyte solution because it lowers the dielectic constant of the solvent and consequently the dissociation of water and of the dissolved materials (14).[15] For this reason, in the presence of alcohol, the color change of an indicator acid, such as phenolphthalein, will occur at a higher pH value, while that of an indicator base, say methyl yellow, is shifted to a lower pH value. Since corresponding changes may be expected in the medium strong or weak electrolytes present in the solution, the total effect of alcohol in a titration is also dependent on their concentration. This considerably complicates the calculation of the correction.

The observation that occasionally the effect of alcohol on indicators is much greater than corresponds to the repression of the dissociation[16] and the further fact that alcohol occasionally causes a color change, was elucidated by Thiel and his co-workers (16, 17, 18, 20) from photographs of the extinction curves of the indicator solutions. They were able to establish both a quantitative and also, particularly, a qualitative change in the extinction, which varied with the individual indicators. Thiel and Springemann (17) point out that an alcohol solution of an indicator is much more sensitive to light than its aqueous solution.

It is well known that the *effect of temperature* on the change of indicators in titrations is due primarily to the decided increase of the dissociation constant of water. The variation of the dissociation constants of the indicators is relatively of much less significance.[17]

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[14] See the observations on Congo red by Michaelis and Rona (11); compare also the colloid chemical considerations of the behavior of Congo rubin by Ostwald (12).

[15] See Michaelis and Mizutani (14).

[16] Thiel [(75) p. 29]; Wegscheider (15); compare also (14) where it was found that the negative logarithm of the dissociation constant of phenolphthalein in 90% alcohol is 12.6 as opposed to 8.6 in water.

[17] It has been shown by Neumann (13) that the salt error becomes less with rising temperature.

THE TITRATION ERROR

General Considerations of the Use of Indicators in Acidimetry and Alkalimetry

The choice of an indicator is made primarily on the basis of the pH value at the equivalence point of the reaction in question. The pH is fixed by the hydrolysis of all the salts present in the solution, and in certain cases, by the weak acids or bases produced during the titration of a salt (sodium carbonate, borax, ammonium chloride). Both these factors are affected by the electrolyte- or alcohol content of the solution.[18] An illuminating picture of the change of the pH value of the solution during a neutralization, and of the position of the equivalence point is given by the graph of a potentiometric titration (Fig. 1). This shows that 0.1 N acetic acid has a pH value which lies at the beginning of the transition interval of methyl yellow, and that after the addition of only a little alkali, this pH value rises considerably because of the repres-

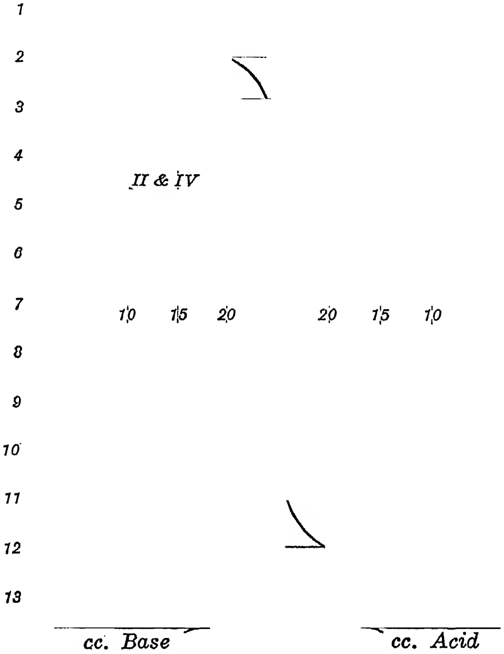

Fig. 1 Change of pH of the Solution During the Titration

I. Titration of 25 cc. of 0.1N HCl with 0.1N KOH.
II. Titration of 25 cc. of 0.1N acetic acid with 0.1N KOH.
III. Titration of 25 cc. of 0.1N HCl with 0.1N NH_4OH.
IV. Titration of 25 cc. of 0.1N acetic acid with 0.1N NH_4OH.

---

[18] The striking increase in the acid character of carbonic acid in the presence of neutral salt is discussed by Szyszkowski (21, 22) and Richter (26).

sion of the dissociation of the acetic acid by the acetate ions that have been formed. The course of Curve III, which represents the titration of ammonia with hydrochloric acid, shows that the conditions are quite analogous with respect to the change of phenolphthalein. It is well known that methyl yellow and phenolphthalein respectively, should not be used in these two cases.

On the other hand, with the aid of the dissociation constants of acids and bases, and if necessary including the activity coefficients, it is possible to calculate approximately the hydrolysis of the salts formed and also the effect of the very weak, non-titratable acids and bases. The ground work for this was given by Bjerrum in his treatment of the titration error (74).[19]

If the pH value at the equivalence point is known it may be advisable to use as a comparison solution during the titration a buffer solution of the same pH containing the same quantity of the indicator (74). Or it may be more satisfactory and more convenient to make up a solution of the salt produced in the titration, and to add to this all the other materials which will be present at the end of the titration [(76) vol. 2, p. 98]. An exact definition of the end point, assumes, of course, that the equivalence point lies in the transition interval of the indicator used.

The procedure preferred by Lunge [20] suffices, in many cases, for all practical purposes. Its salient points are given in the following quotations: "it is obvious that under all conditions, the indicator used when standardizing the acid must be the same as that to be employed later in actual practice." "If a standard acid and an alkali which has been standardized against it are to be used regularly with methyl orange, this indicator must be used in the standardization against sodium oxalate (or carbonate). If, however, phenolphthalein is to be carried to a pink in the ordinary way with standard solutions then, of course, this indicator must have been employed in the standardization." To this Berl adds that "standard solutions which at the standardization were titrated into the base should later be used only for titration into base and to the same shade of the indicator."

Since in this method the titration is carried not to the pH value of the equivalence point but to the color change of a few indicators of extensive applicability, the above principles take into account the transition range of an indicator but not, however, the peculiarities of the neutralization reaction taking place. This is evident, for instance, even in the exact titration of alkali with hydrochloric acid on the one hand, or with sulfuric acid on the other, particularly when dilute solutions are used (see p. 12; compare also the titration of borax, p. 14). Just as little account is taken of the neutral salt effect. This procedure, therefore, is not suitable when greater degrees of accuracy are demanded. It has the practical disadvantage that the same acid or basic solution must be given a different titer for every indicator: "practical titer."[21]

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[19] See also (76), vol. 1, p. 122.

[20] Lunge (68); Berl-Lunge (79); Kolthoff (76), vol. 2.

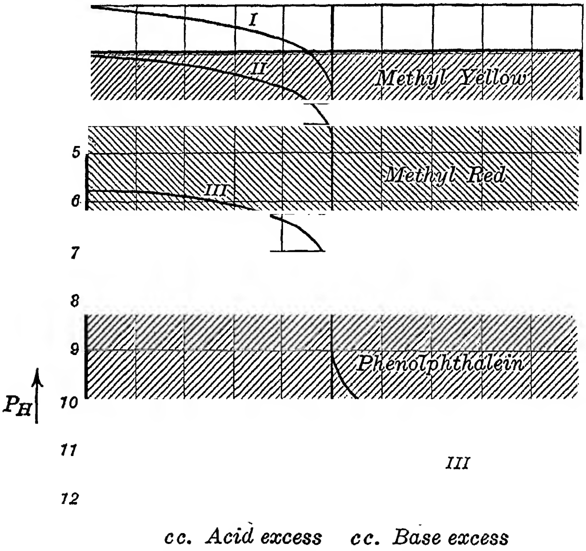

FIG. 2 Change of pH of the Solution at the End of the Titration

I. In the titration of 50 cc. of 0.2*N* HCl with 0.2*N* KOH.
II. In the titration of 50 cc. of 0.02*N* HCl with 0.02*N* KOH.
III. In the titration of 50 cc. of 0.2*N* acetic acid with 0.2*N* KOH.

The method of titration to be described was devised by Böttger (23)[22] and has been tested over a long period of years in the checking of Fixanal solutions. It avoids the above sources of error in a simple way and consequently makes possible the attainment of greater accuracy.

THE APPLICATION OF INDICATOR CORRECTIONS[23]

In this procedure, the titration end point is so chosen that it still lies within the range of the rapid change of the pH value at the equivalence point (Fig. 2) but a difference, conditioned by the indicator, between the equivalence and the change point is deliberately taken into account.

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[21] See also Mika (34).

[22] See also Bjerrum [(74), p. 73].

[23] See particularly (23) to (27).

Then the necessary correction is determined for closely defined titration conditions, including all the materials present in the solution at the end of the titration, and this correction is applied both in the standardization and in the titration. The resulting titer of the standard solution is "absolute," since it is entirely independent of the type of indicator used.

This procedure does not require an indicator whose transition range includes the equivalence point. It is important, however, particularly when working with dilute solutions, to closely fix the shade to which the titration is to be carried. Since dilute indicator solutions do not have a sufficiently stable color, it is best to prepare the "standard shade" with the aid of colored inorganic salts. This reference solution may be used for several weeks and can be prepared easily at any time from the stock solutions. Details will be given in the examples to follow.

With end volumes of 100 cc. the color comparison can be made very well in 300 cc. Erlenmeyer flasks, whose walls should be as free from striations as possible. Obviously flasks of the same shape must be used both for the "standard shade" and for the titration. If all the measurements are made by weight in order to avoid errors due to temperature, drainage and reading, after some practice it is possible to carry out titrations with a maximum error of 0.05% when 40 g. of 1 N to 0.2 N[24] standard solution are consumed. This is especially true if the sample to be tested is also measured from weight burettes, thus permitting titration back and forth. More detailed discussions of several examples follow.

The Titration of Sodium Carbonate with Hydrochloric Acid. Methyl yellow, because of its slight sensitivity to carbonic acid and its easily recognizable change, is used as indicator in a concentration of 0.5 cc. of 0.01% alcoholic solution per 100 cc. of final titration volume.

The standard reference solution is prepared by diluting 8 cc. of 0.001 M (0.29 g. per 1000 cc.) potassium bichromate solution and 40 cc. of 0.01 M (3.95 g. per 100 cc.) cobalt ammonium sulfate solution to 100 cc. According to Schmitt [(27) p. 231], the color of this solution matches that of methyl yellow at a pH of 3.8.

To determine the correction, 100 cc. of a pure sodium chloride solution of approximately the same concentration as will be present at the end of the titration, is treated with the volume of indicator solution given above and titrated to the standard shade with 0.1 N acid. An excess or deficit of acid amounting to 0.010–0.015 g. is easily discernible. The acid consumed corresponds to the correction: it amounts to 0.136 g. of 0.1 N HCl for 0.1 *N* NaCl and to 0.110 g. for 0.5 *N* NaCl. Obvioulsy this correction must be recalculated in terms of the concentration of the acid used in the titration before subtracting it from the total consumed.

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[24] Compare Lunge (68)

The *carbon dioxide* present in the solution at the end of the titration of the carbonate influences, to a slight degree, the acid consumption and in exact titrations this may not be disregarded. This effect is due to the electrolytes which increase the dissociation constants of the carbonic acid. For example if 0.1 *N* sodium carbonate is titrated with hydrochloric acid in the presence of methyl red, which is considerably more sensitive to weak acids, the volume of acid consumed is decreased 3–4% because of the carbonic acid. The color change in this case is far from sharp.[25] The experiments of Richter (26) show that it is not advisable to include this error in the correction, because the quantity of dissolved carbonic acid at the end of the titration is not constant enough. Consequently, an excess of 1–3 drops of hydrochloric acid beyond that required to produce the standard shade is added to the carbonate solution in the presence of about one-third the necessary quantity of indicator. The solution is then boiled for a short time (funnel on the flask). After cooling the solution to room temperature,[26] the rest of the indicator is added and the titration carried to an exact end point. The above correction is subtracted from the acid consumed in this procedure.

The same correction holds for methyl yellow in the *titration of hydroxides*. In this case, the carbon dioxide may be disregarded.

If the same standard shade is always used, it is possible to employ the same corrections also in the *determination of hydrochloric acid* with hydroxides, recalculating to the equivalent quantity of base, if necessary.

The Titration of Sulfuric Acid with Alkaline Hydroxides and Vice Versa. Methyl yellow can also be used as indicator when titrating sulfuric acid with alkali hydroxide, particularly if a 1 *N* solution is used. With the same standard shade that was employed in the carbonate titration, the *indicator corrections* for the alkali sulfate solutions are quite different from those for the alkali chloride solutions. These indicator corrections, if the titration is carried to the standard shade, are:

0.5 *N* Na_2SO_4 consumes 0.044 g. of 1 *N* H_2SO_4

0.1 *N* Na_2SO_4 consumes 0.140 g. of ..2 *N* H_2SO_4

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[25] The writer does not agree with the statements of Biltz and Biltz in their "Ausführung quantitativer Analysen," Leipzig 1930, p. 121.

[26] See (26) concerning the influence of temperature on the indicator constant.

(The same values are obtained if the corrections are determined for sodium sulfate with hydrochloric acid.) Accordingly, in the determination of sulfuric acid, the consumption of base is too little by an amount equivalent to these values.

The difference in the corrections for chloride and sulfate solution is to be ascribed, primarily, to the slight dissociation of sulfuric acid in the second stage [dissociation constant $= 2 \times 10^{-2}$ at 18° C.] [27] This results in the formation of HSO_4^- ions and therefore, in a considerable buffering of the acid added, which of course is somewhat weakened by the effect of the ions in the solution upon the dissociation constant of the HSO_4^- ions.

The following figures give a clear picture of the extent of this buffering: a definite change in the shade of methyl yellow with 0.1 *N* and 0.5 *N* NaCl is obtained by adding 0.010–0.015 g. of 0.1 *N* HCl, whereas with 0.1 *N* Na_2SO_4 it is necessary to add 0.020–0.030 g. of 0.1 *N* HCl, and in the case of 0.5 *N* K_2SO_4 about 0.07 g. is required.

Since the color change of methyl yellow is by no means sharp with 0.2 *N* or even 0.1 *N* solutions, Böttger recommends for accurate titrations of sulfuric acid in more dilute solutions methyl red, which changes at the higher pH range (4.4–6.2). If 0.18 cc. of 0.05% alcoholic solution of the indicator is used per 100 cc. end volume, the same shade can be used for the turning point as with methyl yellow. Under these conditions, a very sharp color change may be obtained, as little as 0.003–0.005 g. of 0.1 *N* HCl sufficing. Of course, the greater sensitivity of methyl red to carbon dioxide (see p. 12, footnote 25) must be taken into account as was done in the titration of carbonate, i.e. the solution made slightly acid as compared with the standard is *boiled* before the titration is carried to its conclusion. It must be remembered that when solutions containing an ammonium salt and slightly acid to methyl red are boiled, an appreciable loss of ammonia is to be expected.

The indicator correction, which likewise, must be determined after boiling the solution, is for

0.1 *N* alkali sulfate solution, 0.022 g. of 0.1 *N* HCl

The corresponding value for

0.1 *N* KCl is 0.013 g. of 0.1 *N* HCl

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[27] Landolt-Börnstein, Physikalisch-chemische Tabellen, 5th edition.

The Titration of Borax. In the titration of borax, which is so often recommended for the standardization of acids,[28] all of the weak acid liberated during the titration remains in the reaction system, in contrast to the carbonate determination. Consequently, when determining the indicator correction, in addition to the sodium salt, the corresponding quantity of boric acid must be dissolved in the final titration volume. The potassium bichromate-cobalt ammonium sulfate solution mentioned on p. 11 can be used as a color standard. Table II gives a number of these corrections. (These hitherto unpublished figures are the writer's own findings.)

TABLE II

No.	Composition of the solution at end of titration	Corrections in g. 0.1*N* solution
		for methyl yellow:
1	0.5 *N* KCl; 1 mole H_3BO_3	2.53 g. KOH (0.120 g. HCl)*
2	0.1 *N* NaCl; 0.2 mole H_3BO_3	0.125 g. HCl (0.135 g. HCl)
3	0.1 *N* Na_2SO_4; 0.2 mole H_3BO_3	0.235 g. HCl (0.280 g. HCl)
		for methyl red:†
4	0.1 *N* NaCl; 0.2 mole H_3BO_3	0.32 g. KOH (0.013 g. HCl)
5	0.1 *N* Na_2SO_4; 0.2 mole H_3BO_3	0.32 g. KOH (0.024 g. HCl)
6	0.05 *N* NaCl; 0.1 mole H_3BO_3	0.039 g. KOH
7	0.05 *N* Na_2SO_4; 0.1 mole H_3BO_3	0.061 g. KOH
		for methyl orange:
8	0.1 *N* KCl; 0.2 mole H_3BO_3	0.046 g. HCl (0.060 g. HCl)

* The figures in parenthesis are the corrections in the absence of H_3BO_3.
† In all determinations using methyl red the CO_2 was boiled out.

It may be seen from these figures, particularly experiments 1, 4, and 5, that the boric acid exerts a considerable influence on the titration end point;[29] this evidences itself by a decided *buffering* of the alkali added and the consequent blurring of the color change. Therefore, titrations under the conditions obtaining in these three experiments should be avoided. In the determination of the correction for 1 *N* solutions (No. 1) there appeared also a striking *change in the color intensity of the indicator:* 0.4 cc. of 0.01% methyl yellow solution instead of 0.5 cc. sufficed for 100 cc. Accordingly, when greater accuracy is required 0.2 *N* borax solution is titrated best in the presence of methyl yellow or methyl orange (Nos. 2 and 8) and 0.1 *N* solution in the presence of methyl red (Nos. 6 and 7), with due regard for the respective corrections. In this case also, the change of methyl yellow with hydrochloric is sharper than with sulfuric acid.

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[28] See for example, v. Bruchhausen (69) and Kolthoff (70); for the earlier literature see Kolthoff [(76) vol II, p. 96].

[29] Compare Kolthoff (71) concerning the formation of more strongly acid polyboric acids in concentrated boric acid solutions.

The Use of Indicator Corrections Under More Special Titration Conditions. (a) *The acidimetric determination of oxalic acid by the method of Bruhns*(72) is an example of a titration in which there are present both an excess of foreign salt and a precipitate. This method offers the possibility of titrating oxalic acid with the aid of methyl yellow or other indicators of about the same transition range. It is common knowledge that these indicators are useless in the direct titration of oxalic acid. To this end, the oxalate ion is precipitated as calcium oxalate by adding an excess of calcium chloride, so that eventually it is hydrochloric acid that is titrated.

Schmitt [(29) p. 286] determined the indicator correction for this case. Calcium oxalate had to be suspended in the reference solution to attain an exact comparison of it with the solution being titrated. Therefore, the reference solution was prepared by treating 50 cc. of 0.2 *N* sodium oxalate solution with 20 cc. of 1 *N* calcium chloride solution and adding 40 cc. of 0.01 *M* cobalt ammonium sulfate and 8 cc. of 0.001 *M* potassium biochromate (compare p. 11). The standard, as before, was placed in a vessel whose size, shape, and kind of glass were the same as that used for the titration.

Duplicating the conditions of the titration, the indicator correction was determined by means of a carbon dioxide-free mixture of 50 cc. of 0.2 *N* sodium oxalate and 20 cc. of 1 *N* calcium chloride made up to a total volume of 120 cc., plus 0.5 cc. of 0.01% methyl yellow. The correction amounted to 0.09 cc. of 0.2 *N* hydrochloric acid.

Schmitt found that the correction for the titration of the same solution to a pink with phenolphthalein (1 drop of 0.1% solution) is 0.06 cc. of 0.2 *N* base. In this instance the excess calcium chloride exerted a marked influence, because a water suspension of pure calcium oxalate had a correction of only 0.03 cc. of 0.2 *N* base.

Table III gives further examples of the effect of other salts on the corrections (the writer's own experiments).

TABLE III

Corrections for Titrations Using Methyl Yellow in the Presence of Neutral Foreign Salts

Composition of the solution at end of titration	g. 0.1 *N* HCl per 100 cc.
0.1 *N* KCl	0.135
0.1 *N* KCl plus 0.4 *N* $BaCl_2$*	0.102
0.1 *N* KCl " 0.2 *N* $BaCl_2$	0.118
0.2 *N* $BaCl_2$	0.113
0.1 *N* Na_2SO_4	0.280
0.1 *N* Na_2SO_4 plus 0.1 *N* KCl	0.208
0.1 *N* Na_2SO_4 " 0.4 *N* KCl	0.171
0.1 *N* NH_4Cl	0.140
0.1 *N* NH_4Cl plus 0.1 *N* KCl	0.126
0.1 *N* $(NH_4)_2SO_4$	0.315
0.1 *N* $(NH_4)_2SO_4$ plus 0.4 *N* KCl	0.179

* Pure $BaCl_2$ solution with methyl red produces a mixed color and not pure yellow, as does NaCl.

(b) Poethke(33) determined the indicator corrections for *phenolphthalein, naphtholphthalein and thymolphthalein in alcoholic salt solutions.*[30] The following figures (Table IV) give a measure of the magnitude of the *corrections for phenolphthalein* (1 cc. of 0.1% alcoholic solution). The final volume was 100 cc. The determinations were carried out with 0.02 *N* sodium hydroxide and recalculated to 0.1 *N* sodium hydroxide. It is plain that in the presence of larger quantities of alcohol even a small concentration of salt affects the error caused by alcohol alone.

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[30] Experiments on *salt-free* alcoholic solutions and phenolphthalein are described in (26).

TABLE IV

Alcohol %	Correction without salt cc.	Correction for 0.005 N NaCl cc.
0	0.03	0.03
20	0.05	0.05
40	0.08	0.07
60	0.12	0.11
80	0.16	0.14
95	0.26	0.16

Analogous studies were made with sodium acetate and potassium palmitate.

The *reference solutions* used by Poethke for the various indicators deserve brief notice. He fixed the slight pink color of the phenolphthalein as that of 0.3 cc. of 0.01 N potassium permanganate diluted to 100 cc. with water [see also (26)]. Although a dilute ammoniacal copper sulfate solution is suitable for the experiments with thymolphthalein *in pure water solution,* some bichromate must be added for the titration in *alcoholic solution,* because the simultaneous presence of alcohol and salt produces a green tinge in the thymolphthalein (see the foregoing, p. 7). A similar observation was made with naphtholphthalein.

(c) Böttger's method for the exact titration of acids and bases was adapted by Mika (30,31,32) to the *micro-titration of strong acids.* The latter has also studied the titration of bases (35,36).

His use of indicator corrections is based on the idea that they may be made independent of the character of the *strong acid* (e.g. HCl or $KHIO_3$) being titrated or of the neutral salt produced, by adding a large excess of foreign salt to the standard solution when it is prepared. In this way, he arrives at a correction which practically is dependent only on the volume of standard solution consumed and on the end volume. The correction for any given case can then be taken easily from a graph. As Mika emphasizes, this applies only for *strong acids,* where the neutral salt error exerts the predominant influence. With *weak acids,* the indicator must be chosen according to the dissociation constants of the acids.

0.01 N $Ca(OH)_2$ which was 1 M with respect to $CaCl_2$ was used as carbon dioxide-free standard solution; methyl red served as indicator. The titration end point color was taken as that which matched a buffer mixture ($pH = 4.86$) containing methyl red, and 0.05 M with respect to citric acid and 0.1 M to disodium hydrogen phosphate.[31]

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[31] According to McIlvaine (73). A detailed compilation of the buffer mixtures recommended by various workers is given in (77).

MIXED INDICATORS

After Luther [(40), see also (38) (39)] first proposed the use of methyl orange in the presence of indigo, numerous applications were made of the idea that indicator color changes can be modified by the addition of colored materials. A brief discussion of the special characteristics of these mixed indicators with reference to the detection of the titration end point is given here. In no case is the transition interval of an indicator changed by the addition of another material, no matter whether or not the latter exhibits a color change at the same time. The added material only alters the subjective color impression because of a change in the total extinction of the solution.

The volumetric application of mixed indicators was promoted primarily through the desire to attain *greater contrast in the colors in the transition interval* of the most commonly used indicators, especially the azo-indicators (methyl orange, methyl yellow, etc.), so that a titration could be carried to a given end point more conveniently and more surely without the use of comparison solutions, or with a more dilute titrant in the face of strong buffering.

In this respect, the mixtures, for instance, of blue dyes and of indicators which change from yellow through orange to red and which are quite insensitive to changes of pH value in the given transition interval, have proved themselves quite useful. The colors yellow and red which are contiguous in the spectrum, are, when in *suitable mixtures,* changed to the approximately complementary colors, green and violet, which are separated by a gray shade. Blue materials particularly recommended for such additions are indigo solution (40, 41)[32] xylene cyanol F F (45) and methylene blue (50, 53).[33] The writer's studies show that an agreement of several hundredths of one per cent can be obtained without the use of comparison solutions in titrations of 40 cc. of 0.2 *N* base against HCl in the presence of methyl yellow and methylene blue. The titrated solution turns deeper blue after short standing.

The exact valuation of this kind of titration requires, of course, an *indicator correction* just as much as those employing single indicators. This correction must also be determined for the shade chosen as an end point, using throughout an indicator mixture of the same composition. For example if 100 cc. of 0.1 *N* KCl is present at the end of the titration, and if the titration in the presence of 1.7 cc. of 0.01% methyl yellow and 0.17 cc. of 0.1% methylene blue solution has been continued until the green changes to gray, 0.17 g. of 0.2 *N* HCl above that equivalent to the base will be consumed. Moerk (41) does away with most of the titration error by adding the mixed indicator to 100 cc. of distilled water, and treating this solution with acid or alkali until the end shade is reached. To 50 cc. of this he adds the solution being investigated and both solutions are titrated then to the same shade. This procedure of course neglects the neutral salt error.

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[32] Commercial indigo solution as well as indigo carmine, solid or paste, frequently contain considerable sulfuric acid, as residue from their preparation, and consequently react strongly acid.

[33] See also Kolthoff [(76), vol. 2, p. 64].

The conditions are quite similar if an indicator is used in the presence of another with about the same indicator exponent.[34] Other reasons for the use of mixed indicators are that they make possible titrations *in artificial light* (45), *the titration of weakly colored solutions* (40), and finally the more easy detection of the approach of the end point if a *"pre-indicator"* has been added (51, 52). Details concerning the behavior of quite a number of mixed indicators may be found in [(76) vol. 2, p. 6]; [(77), p. 178] and [(79), p. 325]. Extensive references to the literature on the use of mixed indicators are given in the bibliography.

FLUORESCENT AND TURBIDITY INDICATORS

Recently two new groups of indicators have been recommended for special acidimetric titrations.

(a) *The fluorescent indicators* are related to the ordinary acidimetric color indicators. However, a change of the pH value of the solution produces in them no color change, but a fluorescence appears or disappears. In order to make this easily perceptible or, in some cases, to produce it, the solution must be sufficiently irradiated with ultra violet light. Holthof (62) has recommended for this a simple apparatus, the "callophane." Fluorescent indicators for pH values from −0.3 to +11 are now known (63). The transition intervals are about as long as those of the usual indicators. Fleck, Holness and Ward (66) found that in addition to purely organic compounds, magnesium-8-oxyquinoline may also be used at about pH = 7.

The particular significance of these indicators is that they may be used in even highly colored and turbid solutions. Malowan (64) recommends them in the titration of colored foods, of extracts of plant parts and suspensions of ash, clay or powdered carbon in hydrochloric acid and also for soil investigations.

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[34] Mixtures of several indicators whose change occurs in different pH intervals are of less importance for titrations than for colorimetric pH determinations. The mixed indicator of Chevalier, Progrés agricole viticole *97*, 354 (1932); Chem. Ab. *26*, 6048 (1932) is quite good for this purpose.

(b) Naegli (56) called attention to the possibility of using *turbidity indicators* in acidimetry. The basis for this is that certain colloidal systems go over into coarse dispersions at definite hydrogen ion concentrations. Weak, slightly soluble acids of high molecular weight prove quite suitable for such titrations. The narrowness of the flocculation intervals is of particular importance; they embrace only 0.1–0.2 pH units. As a result, even when the neutralization curve is quite flat, as in the titration of very weak acids, a distinct end point is obtained. The flocculation points of the indicators found by Naegli lie mostly in the small interval of pH = 10.5–11.5. Details are given in (65).

The bibliography gives extended documentation concerning these two types of indicators.

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PART II

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT

BY

N. HOWELL FURMAN

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT

INTRODUCTION

THE use of acidified solutions of ceric salts as volumetric oxidizing agents was suggested long ago (1–4), but only in recent years have the applications of ceric sulfate been systematically studied by Atanasiu (5–6), by Willard and Young (56–57), by Furman (71–82) and their collaborators.

Quadrivalent cerium is a powerful oxidizing agent in acidified solution; the normal oxidation potential is 1.46 volts in *N* sulfuric acid or 1.443 volts in 2 *N* sulfuric acid at 25° C., referred to a hydrogen electrode in the same acid (37). Ceric sulfate cannot be employed in faintly acid or neutral solutions because slightly soluble basic ceric salts are formed. In concentrated alkali carbonate solution, cerous salts are completely oxidized by mild oxidizing agents, potassium ferricyanide, for example (38). Perceric salts are formed by the action of atmospheric oxygen on cerous salts in alkaline media. Ceric salts, as contrasted with permanganate are, therefore, useful as volumetric oxidizing agents only in acid solution, best in 0.5 *N* or higher concentrations.

The chief advantages of standard ceric sulfate solutions are: (1) Stability at even boiling temperatures; (2) Usefulness in titrating solutions that are acidified with hydrochloric acid; (3) Simplicity of the reactions, there being only one possible reduction product, namely Ce^{+++}:

$$Ce^{++++} + e \rightleftharpoons Ce^{+++}$$

This fact often makes ceric sulfate superior to potassium permanganate. The latter, as is well known, may be reduced, depending upon the conditions, to various products, for instance Mn^{IV}, Mn^{III}, Mn^{II}, etc.

PREPARATION OF CERIC SULFATE SOLUTIONS

Preparation from Pure Ceric Salt. The most convenient source of such solutions is anhydrous ceric sulfate [formula weight 332.25 (39)]. Ceric ammonium sulfate, $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$ (formula weight 632.5) is also excellent.

A solution of any desired normality may be prepared by dissolving the calculated quantity of the salt, based on analysis, in 500 cc. of 1–2 *N* sulfuric acid and diluting with water to one liter. (The final concentration of acid should be between 0.5 and 1 *N*). If there is an insoluble residue, the solution is filtered and then standardized. (See "Standardization," p. 29).

Preparation from Ceric Oxide, CeO_2 (formula weight 172.13). Both crude and purified ceric oxide are on the market. The purity of the oxide must be known approximately. The purer grades of oxide (85–100%) are treated with hot, concentrated sulfuric acid in amounts sufficient to dissolve the oxide (40) and make the solution 1 *N* in sulfuric acid after dilution to the final volume. The calculations are based on the reactions:

$$CeO_2 + 2H_2SO_4 = Ce(SO_4)_2 + 2H_2O$$

$$R_2O_3 + 3H_2SO_4 = R_2(SO_4)_3 + 3H_2O$$

Here R may be Ce, La, Pr, Sa, etc. The atomic weight of cerium may be used for that of R without great error. About 1 hour is required to transform 50–100 g. of finely powdered oxide into yellow ceric sulfate, $Ce(SO_4)_2$, which is almost insoluble in the acid. When the reaction is completed, the mixture is cooled, poured into cold water and diluted to the desired volume. Insoluble matter may be unchanged cerium oxide, silica, etc., and is removed by filtration. Less pure grades of oxide (50–85% CeO_2) dissolve easily at 120° C. in a mixture of equal parts of water and concentrated sulfuric acid. It is advisable to stir the mixture mechanically during the heating (56, 63). After the reaction is completed, the solution is diluted to the desired volume. The cruder grades of oxide contain the oxides and carbonates of other rare earths (La, Pr, Sa, etc.), usually some fluoride, phosphate and also ferric oxide. It is well to allow the solution to settle for about 8–10 days. The solution is decanted or filtered before standardizing. The sulfates of the other rare earths in no way affect the usefulness of the solution. A small amount of ferric ion is without harmful effect in most of the applications of the reagent (see, however, uranium, p. 43). According to Knoche, cerous carbonate or oxalate can be used as the starting material in the preparation of ceric sulfate solution. The carbonate is converted into ceric oxide by strong heating, the oxalate by gentle ignition.

Preparation from Commercial Cerous Oxalate. Rare earth oxides prepared from the commercial oxalate, $Ce_2(C_2O_4)_3.10H_2O$ by gentle ignition of the oxalate, contain only 45–50% of ceric oxide. If it is desired to concentrate the cerium in this, the oxides are converted into the nitrates and the cerium is separated, for the most part, from the other rare earths, either by the method of Bunsen (41) which consists of repeated evaporations resulting in the formation of basic ceric nitrate, or by the method of James (42) which depends on the formation of basic nitrate bromate, or by the permanganate method of Roberts (43). The more or less pure oxides that are obtained by igniting the basic salts are dissolved in sulfuric acid as has been described in the preceding Section 2.

STANDARDIZATION OF CERIC SULFATE SOLUTIONS

The most convenient primary standards are: arsenious oxide, sodium oxalate, pure electrolytic iron; potassium ferrocyanide or potassium iodide may also be used. Indicators (see p. 32) or the potentiometric method may be used to determine the end point.[1]

Arsenious Oxide as Primary Standard (59). (a) *With osmium tetroxide as catalyst* according to Gleu (7). For approximately 0.1 *N* ceric solutions 0.25–0.35 g. of arsenious oxide is dissolved in a hot solution of 1 g. of sodium carbonate in 15 cc. of water. After cooling and diluting to 80 cc., 20 cc. of 6 *N* sulfuric acid, 0.15 cc. (3 drops) of 0.01 *M* osmium tetroxide solution (0.2555 g. of OsO_4 dissolved in 100 cc. of 0.1 *N* sulfuric acid) and 0.15 cc. of 0.01 *M* o-phenanthroline-ferrous indicator are added and the solution titrated with ceric sulfate. Hydrochloric acid up to 0.1 *N* does not interfere; the deleterious influence of larger quantities of chlorides may be overcome by adding mercuric sulfate. The end-point is sharpest in sulfuric acid solution.

(b) *With Iodine Monochloride as Catalyst.* The primary standard is dissolved and diluted to 80 cc. as described in (a); the solution is then acidified with 20 cc. of concentrated hydrochloric acid. After adding 5 cc. of 0.005 *M* iodine monochloride solution (for preparation see p. 30) the titration with ceric sulfate solution is made at room temperature, either potentiometrically or with the aid of an indicator. If the disappearance of the iodine color in a chloroform layer is taken as indication that the endpoint has been reached, the final acidity, according to Swift and Gregory (8), must be between 3.0 and 4.2 *M*. *o*-Phenanthroline-ferrous indicator is also excellent: 1 drop of 0.025 *M* solution is added and the titration, at room temperature, continued until the red brownish color reappears only slowly after adding one drop of ceric solution. The temperature is then raised to 50° C. and the titration completed at this temperature. According to Willard and Young (68) the indicator color should not reappear within one minute.

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[1] For details see Müller. "Elektrometrische (potentiometrische) Massanalyse," Th. Steinkopf, Dresden and Leipsic, 1932. See also Kolthoff and Furman, "Potentiometric Titrations," 2nd Ed., John Wiley and Sons, New York, 1931.

Sodium Oxalate as Primary Standard. The reaction:

$$C_2O_4^{--} + 2\ Ce^{++++} = 2\ CO_2 + 2\ Ce^{+++}$$

proceeds quantitatively, but it is slow at 70–90° C. in solutions containing 5 cc. of concentrated sulfuric acid per 50–100 cc. (6, 71). It is much better to acidify with hydrochloric acid (56).

PROCEDURE

(a) *Potentiometric Indication.* The weighed sample of sodium oxalate is dissolved in water, 10 cc. of concentrated hydrochloric acid added and the solution diluted to 100 cc. The solution is heated to 90–100° C. and immediately titrated with ceric sulfate. The titration may also be made at room temperature, if 5 cc. of 0.005 *M* iodine monochloride solution is added.

(b) *o-Phenanthroline-Ferrous-Ion Indicator* (68). The sodium oxalate taken should be equivalent to 25–35 cc. of the ceric solution. The oxalate is dissolved in water, 15–25 cc. of concentrated hydrochloric acid, 5 cc. of 0.005 *M* iodine monochloride solution, and 0.05 cc. of 0.25 *M* o-phenanthroline-ferrous indicator added. The solution is kept between 45–50° C. during the titration. At the end point the indicator slowly changes from reddish to practically colorless (very pale blue). The pink color must not reappear within one minute.

(c) *Methylene Blue Indicator* (56). The sodium oxalate solution should contain per 100 cc., 10 cc. of 0.005 *M* iodine monochloride and 10–20 cc. of concentrated hydrochloric acid. Two drops (0.1 cc.) of 0.1% aqueous solution of methylene blue are added within 0.2–0.3 cc. of the end point. The titration is made at room temperature. A pink that changes to blue again in 5–10 seconds indicates the end point. The potentiometric method is excellent for this titration.

Preparation of 0.005 *M* Iodine Monochloride Solution. Dissolve 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and add 250 cc. of concentrated hydrochloric acid immediately. The end point is determined electrometrically or with the aid of chloroform. If needed, some iodide or iodate solution is added (56). At the equivalence point, one drop of very dilute iodate solution causes a sharp rise in potential or, if chloroform is used the solution is sharply decolorized, and one drop of an equally dilute iodide solution will restore the color.

Electrolytic Iron as Primary Standard. Pure iron prepared electrolytically or obtained from iron carbonyl is excellent (44). A weighed quantity of pure iron sufficient to consume 35–50 cc. of the ceric solution is dissolved in a mixture of 10 cc. of concentrated hydrochloric acid and 5 cc. of water. The reduction of the ferric iron is effected in the usual way by 0.5 N stannous chloride solution; after cooling and diluting, the excess of the latter is oxidized by adding 5 cc. of saturated mercuric chloride solution. The titration may be conducted potentiometrically or various indicators may be used.

o-Phenanthroline-Ferrous-Ion as Indicator (68). One drop of 0.025 M indicator solution is used; the titration is made at room temperature.

Diphenylamine, Diphenylbenzidine, Diphenylamine Sulphonic Acid. These indicators require the presence of 5 cc. of phosphoric acid (sp. gr. 1.7) per 100 cc. of solution. 0.03–0.05 cc. of 0.1 M indicator is used. The end point change is from greenish to deep blue. The reaction must be carried out slowly near the end point. The indicator correction, 0.05 cc., should be subtracted from the volume of 0.1 N ceric solution (compare also Part VI, p. 159).

Eriogreen, erioglaucin and methyl red may also be used (76). With 0.1 N solutions the correction is negligible (for details see "Determination of Iron," p. 37).

The oxidation of ferrous iron by the oxygen of the air is said to cause an error of 1 part in 1000 (57). If more precise results are desired, air must be excluded (compare also p. 179).

Other Standard Substances. Pure potassium iodide or potassium ferrocyanide may be used. For details of the titration see "Determination of Iodide," p. 38, or "Determination of Ferrocyanide," p. 38.

THE STABILITY OF CERIC SULFATE SOLUTIONS

Solutions of ceric sulfate in 0.5–1 N sulfuric acid are very stable at room temperature (63, 71). Those between 0.01 and 0.1 N remain unchanged for almost a year; the change of the titer amounts to about 1 or 2 parts per 1000. Vanossi and Ferramola (11) report that light decomposes 0.001 *N* ceric sulfate solution. It is advisable to shield the solutions of all strengths from bright sunlight.

Stability at the Boiling Point. Ceric solutions containing 15–20 cc. of sulfuric acid (sp. gr. 1.5) per 100 cc. are stable for 5 hours at the boiling temperature. (The volume is kept constant by adding water). In the presence of 5 cc. of nitric acid (sp. gr. 1.42) and 10 cc. of sulfuric acid (sp. gr. 1.5) per 100 cc., no perceptible reduction of the ceric sulfate occurs during 1 hour, at the boiling point. A ceric solution containing 5 cc. of 70% perchloric acid and 10 cc. of the foregoing sulfuric acid was unchanged after being boiled for 1 hour (63). Ceric solutions are therefore more stable than potassium permanganate solutions of the same normality.

INDICATORS FOR TITRATIONS WITH CERIC SULFATE

When the products of oxidation are colorless, as in the case of oxalic acid or hydrogen peroxide, the color of ceric ion serves to indicate the end point. The yellow color is not very intense and a correction must be applied. If the ceric solution contains ferric ion, this method cannot be used in hydrochloric acid solution.

The classical potentiometric method developed by Böttger (45), Behrend (46) and Crotogino (47), as well as any of the simplified methods may be used with excellent results to indicate the equivalence points of titrations with ceric sulfate (footnote, p. 29).

When iodine monochloride is used as catalyst, the disappearance of the iodine color in a layer of carbon tetrachloride or chloroform gives a sharp end point indication. This method is valuable in the determination of arsenic or of iodide (8, 20).

A number of other indicators, reversible and irreversible, are available for titrations with ceric sulfate. One of the most widely applicable is o-phenanthroline-ferrous-ion, which is truly reversible.

o-Phenanthroline-Ferrous Complex. (9, 10, 68). The stock solution is prepared by dissolving the calculated quantity of o-phenanthroline, $C_{12}H_8N_2.H_2O$ in 0.025 *M* ferrous sulfate solution. In the formation of the complex, 3 molecules of o-phenanthroline combine with one ferrous ion. The indicator change is:

$$\underset{\text{intense red}}{Fe(C_{12}H_8N_2)_3^{++}} \rightleftharpoons \underset{\text{pale blue}}{Fe(C_{12}H_8N_2)_3^{+++}} + e$$

The molar redox potential is about 1.14 volts, referred to the hydrogen electrode. At room temperature the ferrous complex is only slowly decomposed by strong acids or by Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, and Cd^{++}. The blue ferric complex remains practically unchanged by a small excess of a strong oxidizing agent. When a reducing agent is added, the blue complex, at the equivalence point, changes sharply into the reddish ferrous complex. The indicator is suitable for titrations of $C_2O_4^{--}$, Fe^{II}, As^{III}, Sb^{III}, $Fe(CN)_6^{----}$, $MoCN)_8^{----}$, Mo^V, Te^I, U^{IV} or H_2O_2 with Ce^{IV}, and of Ce^{IV} with Fe^{II}, H_2O_2 or NO_2^-; in the latter case the indicator is not added until most of the ceric salt has been reduced.

α, α′-Dipyridyl (12). Indicator Solution: 0.25 g. of α, α′-dipyridyl in 50 cc. water and 50 cc. concentrated ammonia solution. The indicator is said to give good service in the ferrous micro-titration.

Sodium Diphenylamine Sulfonate (48). This indicator, in certain respects, is superior to the related substances diphenylamine and diphenylbenzidine; notable are the sharpness and the reversibility of the color change, and the fact that tungstic acid does not interfere. The 0.005 *M* (0.01 *N* oxidimetric) solution is prepared by dissolving 0.317 g. of the barium salt in 100 cc. of water and adding 0.5 g. of sodium sulfate. The solution is filtered or decanted to remove the barium sulfate. In titrations with 0.1 *N* ceric solution 0.3 cc. of the indicator solution is used. In the titration of ferrous iron, 5 cc. of phosphoric acid (sp. gr. 1.7) must be present per 100 cc., or the indicator will change too soon because of the oxidizing action of the ferric salt. Phosphoric acid need not be added when titrating hydroquinone, ferrocyanide, etc. A correction of 0.03 cc. is subtracted from the volume of 0.1 *N* ceric sulfate consumed. The titration of 0.01 *N* or 0.001 *N* ferrous solutions with bichromate or vanadate involve the following corrections according to Sarver and Kolthoff (49):

0.005 *M* Indicator cc.	Correction with 0.01 *N* cc.	Correction with 0.001 *N* cc.
0.02	0.02	0.21
0.04	0.05	0.44
0.10	0.18	0.93
0.20	0.34	1.85
0.30	0.51	3.48

These values hold approximately for ceric sulfate also.

If the indicator is oxidized prior to use, the correction is smaller and almost independent of the acid concentration and the volume (69).

Diphenylamine and Diphenylbenzidine according to Knop (50). Stock solutions (0.005 $M = 0.01\ N$ redox) are prepared by dissolving 1.69 g. of diphenylamine in 1 liter of sulfuric acid (sp. gr. 1.84) or 1.68 g. of diphenylbenzidine in 1 liter of a mixture of 9 parts by volume of glacial acetic acid and 1 part of sulfuric acid (sp. gr. 1.84). If the diphenylamine is melted (m.p. 52.9° C) to a clear liquid and the requisite quantity of concentrated sulfuric acid then added, 15–30 seconds shaking will accomplish complete solution.[2] In ferrous titrations, phosphoric acid must be present to prevent oxidation of the indicator by ferric salt. The indicator corrections may be derived from the volume of the oxidizing agent necessary to oxidize the indicator in different titrations of 0.1, 0.01, 0.001 N ferrous solutions. The correction is subtracted from the volume of the oxidizing agent used, or, in the reverse titration, the correction is added to the volume of reducing agent. According to Willard and Young (69) the correction is negligible if oxidized diphenylamine is employed.

Erioglaucin and Eriogreen. The use of these indicators was first proposed by Knop (51, 52) for titrations with potassium permanganate. It was found by Furman and Wallace (75, 76) that either is suitable in the titration of ferrous iron or of hydroquinone with ceric sulfate or vice versa. In the titration of ferrous iron the color change is from greenish yellow to pale rose. The rose colored oxidation product is destroyed by a larger excess of ceric sulfate; hence in the back-titration, the indicator is added only after most of the ceric salt has been reduced. Phosphoric acid is not necessary; mercuric chloride does not affect the action of either indicator.

Stock Solution. 0.1 g. of indicator is dissolved in 100 cc. of water. 0.3–0.5 cc. is used in the titration; the correction is practically negligible with 0.1 N solutions.

Other indicators for titrations with ceric sulfate are: Victoria blue Bx according to Caldwell and Weeks (13); not reversible; color change: blue to pale rose; the indicator cannot be used for ferrous titrations following reduction with stannous chloride. Methyl orange may be used in the titration of antimony or hydroquinone; methyl red in the titration of iron, etc. The color of this indicator is destroyed at the end point (see Determination of antimony, p. 35; of iron, p. 37).

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[2] State, Ind. Eng. Chem. Anal. Ed. *8*, 259 (1936).

Determinations with Ceric Sulphate Solution

INORGANIC SUBSTANCES

Antimony. *Reaction:* $Sb^{III} + 2Ce^{IV} = Sb^{V} + 2Ce^{III}$. Trivalent antimony may be quantitatively oxidized by ceric solution at room temperature with iodine monochloride as catalyst (59) or without a catalyst at higher concentrations of hydrochloric acid (14). The end point may be determined potentiometrically or with indicators. o-Phenanthroline-ferrous indicator is preferable if the catalyst is used, otherwise methyl orange.

PROCEDURE (59). 0.25–0.3 g. of antimony, accurately weighed, or an equivalent quantity of an alloy or other material, is heated with 5 cc. of concentrated sulfuric acid. After reaction is complete, the solution is cooled, 20 cc. of water, 25 cc. of concentrated hydrochloric acid and 1 g. of sodium sulfite, are added. The mixture is heated for 10–20 minutes longer while carbon dioxide is passed through it to remove the sulfur dioxide. The volume is kept constant by adding 6 *N* hydrochloric acid. After diluting to 90 cc. and cooling, 10 cc. of 0.005 *M* iodine monochloride solution is added. The titration may be made potentiometrically with excellent results. If the end point is approximately known, methylene blue may be used as indicator; it must be added 0.2–0.3 cc. before the end point. o-Phenanthrolene-ferrous indicator is better. One drop of the indicator solution is added and the titration finished at 45–50° C. (68).

Rathsburg (14) found that antimonous solutions can be titrated at room temperature without a catalyst if the solution contains 15 volume per cent of concentrated hydrochloric acid. The end point is determined potentiometrically or with methyl orange or methyl red as indicator (0.1% water solution; 0.05 cc. per titration). The oxidation of the antimony was reported to be quantitative, even in the presence of trivalent arsenic. The writer studied this subject because of the discrepancy of the results obtained by several workers (80). He found that the oxidation of trivalent antimony by ceric sulphate is quantitative if the solution contains 1/6–1/3, by volume, of concentrated hydrochloric acid. Methyl orange as indicator and the potentiometric method give good results; methyl red is destroyed too easily by local excess of the oxidizing agent. The results are correct if small quantities of arsenic are present. If the amount of trivalent arsenic is equal to or exceeds that of the trivalent antimony, the findings are too high because some of the arsenic is oxidized.

After the oxidation of the antimony is completed, 10 cc. of 0.005 *M* iodine monochloride solution is added and the mixture diluted to 100 cc.

The arsenic may be determined then with ceric sulfate (see p. 29 and below). It should be emphasized that the successive determination of antimony and arsenic gives correct results only when the absolute and relative concentrations of arsenic are small (80).

Arsenic. Reaction: $As^{III} + 2Ce^{IV} = As^{V} + 2Ce^{III}$. Details of this titration were given under "Standardization," p. 29. The reverse titration: reduction of ceric ion with arsenious ion, has been tested by Lang and Zweřina (15, 16). There are, however, much more convenient methods available for the direct titration of ceric solution, for example, with ferrous sulfate, nitrite, etc. The catalysis of the reaction between Ce(IV) and As(III) by iodide or osmium tetroxide was used by Sandell and Kolthoff (53) for the detection of iodide or osmium.

Lead Peroxide (*indirect*). Lead peroxide, PbO_2, and red lead, Pb_3O_4, react quantitatively with hydrogen peroxide in the presence of nitric acid:

$$PbO_2 + H_2O_2 + 2HNO_3 = Pb(NO_3)_2 + O_2 + 2H_2O.$$

About 0.2 g. of sample is treated with 25 cc. of recently standardized 0.1 *N* hydrogen peroxide solution and 25 cc. of nitric acid (sp. gr. 1.42). As soon as the reaction is complete, the excess of hydrogen peroxide is titrated with standard ceric sulfate solution (see "Hydrogen Peroxide," p. 44, concerning method of determining the end point). The solution of hydrogen peroxide is standardized against standard ceric sulfate solution according to Furman and Wallace (74).

Calcium (*indirect*). Calcium is precipitated as calcium oxalate in the usual way, filtered on a glass or porcelain filtering crucible and thoroughly washed (this procedure is also followed for all the other metal ions that can be precipitated quantitatively by oxalate). The precipitate is dissolved in dilute hydrochloric acid (10–20 cc. of concentrated acid + 50 cc. of water). After adding 5 cc. of 0.005 *M* iodine monochloride solution, the oxalic acid is titrated with standard ceric sulfate. For details, see "Oxalate," p. 30 (56).

Chromium (*indirect*). An excess of ceric sulfate oxidizes trivalent chromium rapidly to the sexivalent condition (62). Several procedures for applying this fact to the determination of chromium in ferro-alloys have been developed. The excess of ceric salt is either determined or else destroyed by a suitable reducing agent. If the excess quadrivalent cerium is reduced, the chromic acid may be titrated with a standard reducing solution, such as ferrous sulfate. Any bivalent manganese present will be partially oxidized, but methods for the selective reduction of manganese are available. Vanadium (IV) is oxidized to vanadic acid, and hence chromic and vanadic acid are titrated together.

The excess of ceric sulfate is titrated with standard sodium nitrite or oxalic acid. Two methods are available for the selective reduction of cerium (IV) and manganese. (1) Addition of an excess of nitrite followed by urea to destroy the nitrite; (2) Reduction of the cerium with azide (NaN_3); the excess of azide is decomposed by boiling. The original (62) should be consulted for details.

Standardization of Potassium Bichromate Solutions according to Willard and Young (70.) A measured excess of standard arsenious solution is added and the excess titrated with ceric sulfate as described on pp. 29 and 36 (59).

Iron. *Reaction:* $Ce^{IV} + Fe^{II} = Fe^{III} + Ce^{III}$. This reaction has been studied by several investigators (6, 17, 25, 57, 71). It proceeds smoothly and rapidly. An excellent end point is obtained by the classical or simplified potentiometric methods. The use of o-phenanthroline-ferrous complex, sodium diphenylamine sulfonate, diphenylbenzidine and diphenylamine has been discussed under "Standardization," p. 31.

Methyl red may also be used (76). Stock solution: 0.2 g. of indicator per 100 cc. of 6 *N* sulfuric acid; 0.25 cc. per titration; 0.05 cc. is subtracted (as correction) from the volume of ceric solution. In the back-titration, 0.05 cc. of the indicator solution is added only after most of the ceric solution has been reduced. Methyl red is oxidized to a yellow or brownish material.[3] Five cc. of phosphoric acid (sp. gr. 1.7) should be added. At the end point the indicator turns violet. A correction of 0.05 cc. is added to the volume of ferrous solution used.

Eriogreen and *erioglaucin* are excellent indicators for the titration of ferrous solutions with ceric sulfate or the reverse (76). Stock solution: 0.1 g. of either indicator per 100 cc. of water. A correction of 0.02–0.03 cc. is subtracted from the volume of the ceric solution for each 0.5 cc. of indicator solution. The color change is from greenish yellow to rose. It is necessary to titrate rather slowly near the end point because the oxidation of the indicator is not instantaneous. Mercuric and stannic ions do not interfere. In the reverse titration the indicator is not added until the yellow ceric color has almost disappeared. The color change is from pink to yellow green. The correction is almost negligible (0.02 cc. of 0.1 *N* solution per 0.5 cc. of indicator solution).

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[3] Methyl red under certain conditions is destroyed by an excess of ceric sulfate. However, the indicator is oxidized first to a material which is yellow in dilute solution and brownish in concentrated solution. If this is immediately reduced with ferrous sulfate a violet material results. This differs from methyl red with respect to solubility in organic solvents. The transformation is not reversible.

α, α'-dipyridyl (12) is reported to be an excellent indicator for microtitrations of ferrous solutions (see p. 33).

The $Ce^{IV} - Fe^{II}$ reaction is the basis for the indirect determination of many substances. See "Chromium," p. 36; "Sodium," p. 40; "Mercury," p. 41; "Tellurous Acid," p. 42; "Organic Acids," p. 45.

Ferrocyanide. *Reaction:*

$$Fe(CN)_6^{----} + Ce^{++++} = Fe(CN)_6^{---} + Ce^{+++}.$$

This reaction has been studied by several investigators (6, 18, 73). Good results are obtained potentiometrically (6, 73), or with indicators: o-phenanthroline-ferrous complex (68), erioglaucin or eriogreen (73), and diphenylamine (19). If the ceric sulfate contains about 1 mg. of ferric salt per 25 cc., as is often the case, colloidal ferric ferrocyanide is formed during the titration; it gives a greenish color to the solution. According to Furman and Evans (73) this color disappears sharply at the end point.

Procedure. The sample of ferrocyanide should consume 25–50 cc. of ceric solution. It is dissolved in 50–100 cc. of 1–3 *N* hydrochloric acid or of 4 *N* sulfuric acid. The titration is made at room temperature, either with one of the indicators mentioned, or potentiometrically. If o-phenanthroline-ferrous indicator is employed, it is better to work in hydrochloric acid solution, as the color change is more distinct. This titration has been used in the indirect determination of sugar (see p. 47).

Someya (18) found that pure anhydrous potassium ferrocyanide is an excellent primary standard for ceric solutions.

The reverse titration gives good results only if 80–97% of the ferrocyanide solution is added all at once. If it is added slowly, some ferricyanide reacts with the excess of ceric ion (73).

Iodide. *Reaction* (1): $2\,Ce^{++++} + 2\,I^- = I_2 + 2\,Ce^{+++}$. The reaction proceeds stoichiometrically in solutions that contain 0–50 cc. of sulphuric acid (sp. gr. 1.25) per 100 cc., or that are 0–0.5 *N* with respect to hydrochloric acid. The reverse titration (Ce^{++++} with I^-) proceeds smoothly in sulfuric acid solution. No visual indicator is known (58).

Reaction (2) : $2\ Ce^{++++} + I^- + Cl^- = 2\ Ce^{+++} + ICl$. Willard and Young (58) found an error of about 5 parts per 1000 in the potentiometric titration; this may be due to loss of iodine. Results accurate within 2 parts per 1000 are obtained if a layer of carbon tetrachloride is used as indicator (20). The final concentration of the hydrochloric acid must be between 4–6 *N*.

According to Willard and Young (58) the presence of bromide makes the potential break less sharp.

$$\textit{Reaction}\ (3) : 2\ Ce^{++++} + I^- + \underset{\text{acetone}}{C_3H_6O} = 2\ Ce^{+++} + \underset{\text{iodo-acetone}}{C_3H_5OI} + H^+$$

Lewis[4] uses this reaction for the direct determination of iodide with ceric sulfate solution. The acetone combines with the iodine liberated. o-Phenanthroline-ferrous indicator serves well.

PROCEDURE. A measured volume or known weight of an iodide solution is placed in a flask and 25 cc. of acetone and 10 cc. of 9 *M* sulfuric acid are added. After diluting to 100 cc., 1 drop of 0.025 *M* o-phenanthroline-ferrous indicator solution is introduced. The titration with 0.1 *N* ceric sulfate solution is carried out as usual. The end point is a sharp change from pink to pale blue. The rose color should not reappear within several minutes.

Potassium (*indirect*). See "Nitrite," p. 40.

Cuprous Salt. See "Reducing Sugars," Copper Method, p. 48.

Molybdenum. (1) POWERFUL REDUCTION. The reduction may be effected by titanous chloride, zinc, lead, or stannous chloride, in an atmosphere of carbon dioxide. After the reduction is complete, the titration with ceric sulfate is made in the same atmosphere. The solution must be hot and must contain 50% by volume of hydrochloric acid, some manganous salt must be present as catalyst. There is a break in potential after Mo(III) has been oxidized to Mo(V); a second jump follows at the completion of the oxidation of Mo(V) to Mo(VI). Compare Stehlik (21) and Takeno (25).

(2) MILD REDUCTION. If a molybdic acid solution that is 2–3 *N* with respect to hydrochloric acid is shaken vigorously for 5 minutes with mercury, the molybdenum will be reduced completely to Mo(V). The

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[4] Lewis, "Volumetric Determination of Iodides," Ind. Eng. Chem. Anal. Ed. *8,* 199 (1936).

suspension is filtered, the residue well washed with 2 *N*. hydrochloric acid, the filtrate diluted to 300 cc. with 2 *N* hydrochloric acid, 2 drops of o-phenanthroline-ferrous indicator added, and the titration with standard ceric solution is made at room temperature (81). Furman and Murray found that the solution may not contain more than 0.25 g. of molybdenum per 300 cc. Excess phosphoric acid, arsenic acid or ammonium salts do not interfere. Small amounts (0.1–1.0 mg.) of copper salts interfere because they catalyze the oxidation by air.

The titration of $K_4Mo(CN)_8$ with ceric sulfate solution may be satisfactorily carried out in the presence of o-phenanthroline-ferrous indicator (82).

Sodium (*indirect*). As is well known, sodium may be precipitated as sodium magnesium triuranyl acetate $[NaMg(UO_2)_3(C_2H_3O_2)_9 . 6\frac{1}{2} H_2O]$ (54), or as sodium zinc triuranyl acetate $[NaZn(UO_2)_3(C_2H_3O_2)_9 . 6H_2O]$ (55). The precipitate is dissolved in cold sulfuric acid [2 cc. H_2SO_4 (sp. gr. 1.84) per 100 cc.] and the uranium reduced by passage through a Jones reductor charged with zinc granules amalgamated with 1–2% of mercury. U^{III} is oxidized to U^{IV} by passing a rapid stream of air through the solution for 5 minutes. A measured excess of standard ceric solution is added. This oxidizes U^{IV} to U^{VI} and the excess ceric salt is measured then with ferrous solution. Eriogreen, erioglaucin or o-phenanthroline-ferrous complex may be used as indicators. The titration may also be made potentiometrically. The method gives excellent results for quantities of sodium between 0.001–0.0200 g., since 1 cc. of 0.1 *N* ceric solution is equivalent to only 0.0003833 g. of sodium. See also "Uranium," p. 43.

Nitrite. *Reaction:*

$$2\ Ce^{++++} + NO_2^- + H_2O = NO + 2\ Ce^{+++} + 2H^+.$$

The direct titration of nitrite solution with ceric sulfate was proposed quite some time ago by Barbieri (4). The end point was taken at the appearance of the color of the ceric ion. The procedure, however, gives incorrect results because of loss of nitric oxide. It is better to place the nitrite solution in the burette and to allow the tip of the burette to dip under the surface of the measured volume of the ceric solution (22, 62). The ceric solution should be at 45–50° C. and be acidified with sulfuric or nitric acid. The potentiometric titration is quite slow near the equivalence point. If o-phenanthroline-ferrous indicator is used, it is added only after most of the ceric salt has been reduced. The color change is from pale bluish gray to pale pink. The reaction has been studied chiefly as a means for the destruction of, or, for the determination of an excess of ceric ion; it can, however, be useful in determining nitrite (62).

Bennett and Harwood (22) have used this titration for the indirect determination of potassium. The potassium cobalti-nitrite, which has been collected in a filtering crucible, is dissolved in 0.01 *N* ceric solution and the excess is titrated with standard ferrous solution. 0.1 cc. of erioglaucin solution (p. 34) is added near the end point.

Mercurous Salt. Univalent mercury may be completely oxidized by heating with a large excess of ceric sulfate for 15–60 minutes. After cooling, the excess is titrated back with standard ferrous solution (67).

PROCEDURE. The mercurous solution containing 0.03–0.09 g. of mercury may contain 10 cc. of sulfuric acid (sp. gr. 1.5) or 5 cc. of 70% perchloric acid per 100 cc. The presence of much nitric acid is undesirable; 5 cc. of nitric acid (sp. gr. 1.42) causes an error of 0.6 mg. of mercury. The solution is treated with 25–50 cc. of 0.1 *N* ceric solution, diluted to 200 cc. and heated just below boiling for 30–60 minutes. After cooling, the back-titration is made with recently standardized ferrous solution. The method gives good results, even when a large excess of bivalent mercury is present. However, if the total mercury content (I + II) exceeds 0.3 g., a blank determination with the corresponding quantity of mercury (II) must be made, since if much of the latter is present, it causes a slight decomposition of ceric sulfate. For the quantities of mercury just specified, the correction amounts to 0.07–0.21 cc. of 0.1 *N* ceric solution. For more than 30–35 mg. of mercury (I), a blank must be run, using the same quantities of reagents and the same procedure as is employed in the assay of the sample.

Hydrazoic Acid (HN_3) and Azides. Many years ago Sommer and Pincas (23) determined hydrazoic acid by measuring the volume of nitrogen liberated in the reaction:

$$2\,Ce^{++++} + 2\,HN_3 = 3\,N_2 + 2\,Ce^{+++} + 2\,H^+.$$

According to Martin (24) the excess ceric solution can be determined iodometrically.

PROCEDURE. The air is expelled from a 500 cc. bottle by nitrogen or carbon dioxide and the solution of the acid or azide is added. A measured excess of ceric solution is introduced, the bottle closed, shaken and then allowed to stand for 5 minutes. Then an excess of potassium iodide is added, and the iodine set free is titrated with standard thiosulfate solution. The chief sources of error are loss of hydrazoic acid by volatilization and the oxidation of iodide by air; the latter reaction is catalyzed by cerium salts. The method cannot be used in the presence of hydroxylamine or hydrazine; ammonium ion does not interfere.

Tellurous Acid (66). Tellurous compounds may be oxidized in the presence of selenious acid or of cupric ion, by heating with an excess (40–60%) of ceric solution. A chromic salt must be added to catalyze the reaction. After cooling, the excess ceric salt is determined with standard ferrous solution.

PROCEDURE. The solution of tellurous acid is treated with 50–100 cc. of standard ceric solution, 10–50 cc. of sulfuric acid (sp. gr. 1.5) and 5–10 cc. of 0.08 *N* chromic sulfate solution. The solution is made up to 200 cc. and boiled for 5–10 minutes. After cooling to 30° C., the excess of quadrivalent cerium is determined. Excellent results are obtained, even in the presence of 0.3 g. of selenium in the form of selenious acid, or 0.3 g. of copper.

Thallium. According to Willard and Young (64) thallous ion (I) is completely oxidized to thallic ion (III) by direct titration with ceric sulfate. If the quantity of thallous ion is small, the reaction is carried out at higher concentrations of hydrochloric acid and the titration is made at room temperature. For example, 0.04 g. Tl as thallous sulfate can be titrated excellently at room temperature if dissolved in water containing 60 cc. of concentrated hydrochloric acid per 200 cc. It is more usual to titrate at 50° C. in the presence of 10–30 cc. of concentrated hydrochloric acid per 200 cc. of solution. This applies to 0.1–0.3 g. of thallous salt. The end point is determined potentiometrically or by the color of the ceric ion; in the latter case, the correction is found from a blank. Finally, o-phenanthroline-ferrous indicator may be employed; the color change is from brownish yellow to clear green. In this case, iodine monochloride (5 cc. of 0.005 *M* solution) is added as catalyst (64). The use of iodine monochloride and the utilization of the iodine color in the chloroform layer as indicator in the ceric titration was proposed by Berry (19). Later studies (26) showed that this method is not satisfactory; the over-consumption of ceric solution is 0.6–2% when the final concentration of hydrochloric acid is 4–8 *N*.

The determination of Tl (I) is reliable in the presence of 0.1 g. of the following substances: Cu^{++}, Fe^{+++}, Cd^{++}, Bi^{+++}, Sn^{++++}, Pb^{++}, Hg^{++}, Zn^{++}, SeO_3^{--}, TeO_3^{--}, AsO_4^{---}, SbO_4^{---}, and Cr^{+++}. With the last, the acid concentration must be high and the temperature low, to prevent oxidation of Cr (III) (64).

Thiosulfate. Furman and Wallace (77) found that standard ceric solutions may be used to determine thiosulfate and for the standardization of thiosulfate solutions. It is also possible to allow the ceric solution to liberate iodine which is then titrated. This procedure is only successful in the absence of air. It is far better to add potassium iodide to the thiosulfate solution and then titrate directly with ceric solution in the presence of starch. During the titration, iodine appears transiently but it reacts rapidly with the thiosulfate.

Procedure. About 0.6 g. of crystallized sodium thiosulfate, or an equivalent quantity of another material, or 25 cc. of approximately 0.1 *N* thiosulfate solution is brought up to 250 cc. or more with water, after adding 0.3–0.4 g. of potassium iodide and 20 cc. of 0.2% starch solution. The mixture is then titrated with ceric solution to the ordinary iodine-starch color change. The solution must be mixed thoroughly during the titration and the strength with respect to thiosulfate must be 0.01 *N* or less.

Titanium. Zinc amalgam reduces titanium (IV) to titanium (III). The solution is protected against atmospheric oxygen and is titrated with standard ceric solution in the presence of diphenylamine as indicator (25).

Uranium. It is well known that uranyl solutions when passed through a Jones reductor (granulated zinc amalgamated with 1–2% mercury) are reduced to a mixture of U(III) and U(IV). The mixture can be titrated potentiometrically (25, 27, 28). The writer and others (78, 79) after studying this reaction, have established the following pertinent facts: the uranium solution is reduced well at room temperature; acetate ion does not interfere; chloride should not be present. If a little iron is present in the ceric solution there is some reduction to iron (II) during the oxidation of U (III) to U (IV) and a slight error is introduced. It is therefore better to oxidize U (III) to U (IV) by passing a rapid stream of air through the solution for 5 minutes.

The reaction: $2\ Ce^{IV} + U^{IV} = U^{VI} + 2\ Ce^{III}$ may be followed potentiometrically, or the end point may be found with o-phenanthroline-ferrous indicator. If more convenient, excess ceric sulfate may be added and the excess determined by titrating back with ferrous sulfate.

Procedure. The uranium compound in 2% sulfuric acid solution (2 cc. of concentrated acid per 100 cc.) is passed slowly through the reductor, followed by 2% sulfuric acid. A rapid stream of air is then passed through the reduced solution for 5 minutes. Only U (IV) is now present, no U (III), and the solution may be titrated with ceric sulfate in any convenient way.

If two potentiometric breaks are desired, U(III) to U(IV), and U (IV) to U (VI), the solution is protected from oxidation by the air by a current of carbon dioxide, and is heated to 80° C. during the oxidation of U (IV) to U (VI).

The reaction is fairly rapid at 50° C. and o-phenanthroline may be used as indicator.

PROCEDURE. The uranium (IV) solution should contain 10–20 cc. of sulfuric acid (sp. gr. 1.5) and 1 drop (0.05 cc.) of 0.025 *M* indicator solution per 200 cc. (68). The titration is made at 50° C.; the color change at the end point is from brownish green to clear green.

See also "Sodium (indirect)" p. 40.

If iron, vanadium and uranium are present in the sample, the potentiometric method must be used. See the books on potentiometric titration referred to in the footnote on p. 29.

Vanadium. The reaction:

$$Ce^{++++} + VO^{++} + 2\ H_2O = VO_3^{-} + Ce^{+++} + 4H^{+}$$

proceeds quantitatively and rapidly at 50–60° C., and even in the presence of chromic and ferric salts, if 10–50 cc. of 0.1 *N* vanadyl solution is treated with 5 cc. of concentrated sulfuric acid or 10 cc. of concentrated hydrochloric acid in a total volume of 25–200 cc.; compare Furman (72). The potentiometric method is used. This procedure may be applied with excellent results to the determination of vanadium in ferro-vanadium (72). Hydrochloric, perchloric or nitric acid do not interfere (61). The titration is applicable also to the determination of vanadium in special steels (61).

Hydrogen Peroxide. As is well known, ceric ion oxidizes hydrogen peroxide in acid solution:

$$2\ Ce^{++++} + H_2O_2 = 2\ Ce^{+++} + O_2 + 2\ H^{+}.$$

Atanasiu and Stefanescu (6) and also Furman and Wallace (74) studied this reaction potentiometrically. Either solution may be placed in the burette. The peroxide solution may contain nitric, sulfuric, hydrochloric or acetic acid in any concentration from 0.5–3 *N*, or even more (74). The end point is also well indicated by the ceric color. However, according to Willard and Young (68) it is better to use o-phenanthroline-ferrous indicator at room temperature both for the titration of hydrogen peroxide with ceric solution or vice versa. In the reverse titration, the indicator is not added until most of the ceric salt has been consumed. The application of this titration to the indirect determination of lead peroxide has been discussed on page 36.

Berry (29) has applied the reaction to the determination of hydrogen peroxide in the presence of Caro's acid and persulfuric acid. An approximate titration is made first with the solution at 0° C. Then cooled ceric sulfate solution sufficient to come within 1 cc. of the end point is placed in a flask, the peroxide mixture cooled to 0° C. added and the titration with ceric solution completed. No indicator other than the ceric color is used. Berry gave only a few check analyses.

Tin. The bivalent tin in reduced solutions of tin and tin alloys can be titrated with standard ceric solution in the presence of hydrochloric acid. Starch-potassium iodide solution or diphenylamine solution can be used as indicator. Compare Basset and Stumpf (30) and also Rudney (31).

ORGANIC MATERIALS

Hydroquinone. This substance may be titrated smoothly with ceric solution; quinone does not interfere. The end point may be determined potentiometrically or by means of methyl red or diphenylamine, etc. (75). The reaction is:

$$2\,Ce^{++++} + C_6H_4(OH)_2 = 2\,Ce^{+++} + C_6H_4O_2 + 2\,H^+$$

Hydroquinone may also be used as the titrant. The hydroquinone solution may contain hydrochloric or sulfuric acid, 0–2 *N*. In the cold, quinone is not attacked by ceric solution. If diphenylamine is used as indicator, the usual correction must be applied. Methyl red is a poorer indicator in this case, but it requires no correction with 0.1 *N* solution.

Organic Acids. It may be seen from Benrath and Ruland's study (32) of the kinetics of the oxidation of tartaric and oxalic acid by ceric sulfate that an excess of sulfuric acid retards the oxidation. Formic acid is one of the oxidation products of tartaric acid and is attacked by ceric sulfate only in direct sunlight. According to Berry (19) only 3.5 atoms of oxygen are consumed per mole of acid in the direct titration of tartaric acid.

Willard and Young (65) have made a thorough study of the determination of several organic acids by heating to 90–95° C. for 30–60 minutes with an excess of ceric solution, followed by cooling and back-titration. Formic, acetic and succinic acids are not oxidized by this procedure, and fumaric and maleic acids to a slight extent only.

Tartaric, malonic, malic, glycolic and citric acids are oxidized; ordinarily formic acid and carbon dioxide are produced. Since formic acid resists further oxidation, the above acids may be determined even though they do not consume integral numbers of equivalents of oxygen per mole (65).

Benzoic, phthalic and salicylic acids are oxidized to a variable extent, according to conditions, so that no procedures can be given for their determination.

The results are summarized in the following Table. The method is empirical, but it gives good results over rather wide ranges of acidity, total volume, excess of ceric sulfate and period of heating at 90–95° C.

DETERMINATION OF ORGANIC ACIDS (65)

Acid			Period of Heating at 90-95°C. minutes	Volumes cc.	Ceric Solution Present during Heating cc.		Weight of Acid Equivalent to 1 cc. of 0.1 *N* ceric solution g.
Tartaric	0.0213–0.1598	15–45	10–60	100–300	30–100	3.6	0.002084
Malonic	0.0173–0.0867	20–80	15–60	80–400	35–100	3.33	0.001563
Malic	0.0338–0.0593	20–60	15–120	200	50–75	4.625	0.001449
Glycolic	0.2005–0.1026	20–60	30–120	100–300	50–75	.975	0.001923.
Citric	0.0500–0.0700	20–75	30–60	110–300	60–100	.925	0.001211

Oxalic Acid. The reaction has been thoroughly discussed under "Standardization," p. 30. If it is desired to determine oxalic and citric acids in mixtures of the two (33), a sample of the mixture is titrated with sodium hydroxide. A second sample is diluted to a suitable strength, such as 0.01, 0.02, or 0.05 *N* with respect to total acid. 25 cc. of the diluted solution is treated with 75 cc. of standard ceric solution (0.1 *N*), 2 cc. of sulfuric acid, 1:1, and heated for 1 hour at 90–95° C. The excess ceric solution is titrated with a standard reducing agent such as ferrous sulfate, oxalic acid, etc. The percentage of citric acid is most conveniently read off from the graph showing the per cent content of citric acid versus cc.'s of 0.1 *N* ceric solution, which was established by Wilkinson, Sipherd, Fulmer and Christensen (33) for solutions containing known mixtures of citric and oxalic acid, and that were 0.01, 0.02, or 0.05 *N* with respect to total acid.

Pyruvic Acid. Pyruvic acid and other α-ketonic acids are oxidized (34) by an excess of standard ceric solution in accordance with the following or another appropriate equation:

$$CH_3\text{-}CO\text{-}COOH + 2\,Ce^{++++} + H_2O = CH_3COOH + 2\,Ce^{+++} + 2\,H^+ + CO_2$$

The excess of ceric solution is then determined with a standard ferrous solution.

Procedure. A sample of pyruvic acid (4–20 mg.) is acidified with sulfuric acid and added to 15 cc. of standard (0.1 or 0.5 *N*) ceric solution. After the mixture has stood for 5 minutes, the excess ceric solution is titrated back with standard (0.05 or 0.1 *N*) ferrous solution. Larger amounts of lactic acid interfere; for smaller amounts a correction can be applied; compare (34).

Reducing Sugars. (1) *Ferricyanide Procedure,* according to Whitmoyer (35). If glucose, fructose or invert sugar is warmed with an excess of potassium ferricyanide solution in sodium carbonate solution, an equivalent quantity of potassium ferrocyanide is produced. The solution is then acidified and the ferrocyanide titrated with standard ceric solution. Alphazurine G (Neptune blue B G) is used as indicator; the color change is from yellow green to brown.

Procedure. 5 cc. of potassium ferricyanide solution (8 g. of the crystallized salt per liter) is placed in a flask along with 15 cc. of water and 5 cc. of sodium carbonate solution (140 g. of $Na_2CO_3.H_2O$ per liter). After 4.5 minutes at 25° C., 100 cc. of the sugar solution is added to the mixture, which is allowed to stand 1.5 minutes and then heated to 80° C. The solution is thoroughly stirred for 1 minute and then allowed to stand for 30 minutes longer at 80° C. The solution is cooled rapidly to 25° C., stirred for 1 minute, and then kept at this temperature for 4.5 minutes. It is then acidified by adding 5.7 cc. of 4.3 *M* sulfuric acid and titrated with 0.01 *N* ceric solution, using a micro-burette. Near the end point, 5 drops of 0.4% aqueous solution of alphazurine G is added as indicator. A blank determination is made upon the reagents and the appropriate correction found; this includes the indicator correction.

The results are good for small quantities of sugar, that is 0.5–0.2 mg.; the accuracy is 0.3–0.4%. An excess consumption of 0.02 cc. of 0.01 *N* ceric solution was found if 18 mg. of cane sugar was present. In the determination of very small quantities (about 0.1 mg.) of reducing sugar, the volume is kept at 20 cc. during the reduction, and at 40 cc. during the titration with 0.002 *N* ceric solution. Chlorides and tartrates do not interfere. A blank determination must be made with acetate and citrate buffers of pH 3.5 and 4.5.

(2) *Copper Method,* according to Stegeman and Englis (36). The reducing sugars are treated in the usual way with alkaline copper sulfate solution. The cuprous oxide precipitate is separated by filtration, washed well and then dissolved in a measured excess of standard ceric solution. The excess is titrated in the presence of o-phenanthroline with recently standardized ferrous sulfate solution.

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PART III

ALKALINE PERMANGANATE SOLUTION AS VOLUMETRIC OXIDIZING AGENT

BY

HELLMUTH STAMM

ALKALINE PERMANGANATE SOLUTION AS VOLUMETRIC OXIDIZING AGENT

EXPERIMENTAL LIMITS OF THE OLDER METHODS OF PERMANGANATE TITRATION

IT IS well known that the simplest form of the permanganate titration in which the material to be determined is treated in an acid medium with permanganate solution until the appearance of a permanent pink indicates the end of the reaction, is not generally applicable. There are many materials which only in an alkaline medium are so oxidized by MnO_4^- ion that a practicable volumetric procedure can be based on this oxidation. For instance, prussic acid in acid solution is scarcely attacked by an excess of permanganate, but in alkaline medium it is oxidized immediately. Sulphide, sulfite, and thiosulfate with acid permanganate give varying mixtures of dithionate and sulfate, with alkaline permanganate, however, sulfate is quantitatively produced. In addition, there are many compounds whose oxidation with permanganate by the customary older procedures is so slow that the titration becomes quite tedious. This is particularly true of organic compounds. Furthermore the auto-decomposition of the permanganate solutions under these conditions renders the procedures inexact. Often it has been recommended that the reaction be accelerated, in such cases, by oxidizing in boiling solution with excess permanganate, and that the quantity of oxygen lost through the unavoidable auto-decomposition of the permanganate in hot solution be determined in a blank. However, Kolthoff[1] quite correctly calls attention to the doubtful value of this procedure. The oxygen loss in the blank may be much less than in the titration because, for instance, of the production in the latter of large quantities of reduction products (MnO_2, etc.) that accelerate the auto-decomposition. For such reasons, Kolthoff rejects hot permanganate titrations as fundamentally unsound. But even if the reaction is carried out in the cold the blank may not be omitted if the reaction times becomes unduly long, as with methanol[2] or hypophosphite[3] (24 hours), or with erythrite and pentaerythrite[4] (48 hours).

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[1] Kolthoff, Die Massanalyse. 2nd Ed., Vol. I, p. 224 (1930); Vol. II, p. 295 (1931).

[2] Kolthoff, *op. cit.*, Vol. II, p. 356.

[3] Kolthoff, *op. cit.*, Vol. II, p. 316.

[4] Kolthoff, *op. cit.*, Vol. II, p. 357.

The writer has described a procedure which makes it possible to oxidize quantitatively such materials with alkaline permanganate solution at room temperature in a few minutes.[5]

PRINCIPLE AND SCOPE OF THE NEW PROCEDURE

Holluta[6] has shown that in the reaction between permanganate and formate the reduction of permanganate in (not too weakly) alkaline solution proceeds in two sharply separated partial reactions: (1) the reduction of permanganate to manganate, (2) the reduction of manganate to manganite. The first of these reactions proceeds much more rapidly than the second; the difference of the velocities increases with rising OH^- concentration. This is the reason that when the alkalinity is sufficient, the manganate takes no part in the oxidation so long as considerable quantities of permanganate are still present. Holluta's measurements indicate that the hydroxyl ion takes a direct part in the reduction of permanganate. He regards the atomic oxygen, which may result from the oxidation of 2 OH^- by permanganate, as an intermediate product of the reaction of MnO_4^- with formate, and thus explains the fact that the measurable reaction in the first part of this conversion ($MnO_4^- \rightarrow MnO_4^{--}$) is of the second order. The actual relations are probably more closely approached if the production of intermediate free hydroxyl radicals is postulated.[7] With this assumption, the effect of hydroxyl ion on the velocity of the two stages of the reduction of permanganate in an alkaline medium may be formulated:

$$(1)\quad MnO_4^- + OH^- \rightleftarrows MnO_4^{--} + OH;$$

$$(2)\quad MnO_4^{--} + 3\,H_2O \rightleftarrows H_2MnO_3 + 2\,OH + 2\,OH^-.$$

With increasing OH^- concentration the equilibrium of the first reaction is shifted toward the right, that of the second toward the left. This agrees with the facts (according to Holluta, even quantitatively) though for the second partial reaction only within certain limits of alkalinity. The appearance of hydroxyl ion on the right side of equation (2) is not conditioned by the reduction of MnO_4^{--}, but by the slight dissociation of H_2MnO_3, therefore, by hydrolysis. Free hydroxyl arising intermediarily may well be the real oxidizing agent in oxidations with alkaline permanganate, insofar as it probably—like hydroxyl ion—has a mobility considerably greater than MnO_4^-. If no oxidizable material is present the very reactive OH radicals, in addition to reacting with MnO_4^{--} (producing MnO_4^- and OH^-), may also react with each other to form water and gaseous oxygen. Thus the "auto-decomposition" of alkaline permanganate proceeds at an increasing rate with rising OH^- concentration.

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[5] Stamm, A new method for titrating with alkaline permanganate solution. Z. angew. Chem. *47*, 191 (1934); *48*, 710 (1935); Determination of the oxidizability of natural waters and sewage. Ibid. *48*, 150 (1935).

[6] *Holluta.* The reaction mechanism of the reduction of permanganate solution and its physical-chemical basis. III and IV. Z. phys. Chem. *102*, 32, 276 (1922); IX, Ibid. *113*, 464 (1924).

[7] The appearance of OH radicals is a common assumption in modern studies of reaction kinetics.

Sackur and Taegener[8] determined the normal potential of the reaction: $MnO_4^- + e = MnO_4^{--}$ to be + 0.61 volt and of the reaction $MnO_4^{--} + 2\,H_2O + 2\,e = MnO_2 + 4\,OH^-$ to be + 0.50 volt (at about 18° C. and in 1 *N* KOH). The difference between these two potentials lies therefore in the same direction as the difference of the velocities of the two partial reactions just discussed.

The principle of the new procedure developed by Stamm for titrations with alkaline permanganate solution is that the oxidation of the material being determined involves only the first, very rapid partial reaction of the reduction of the permanganate, that is, the conversion $MnO_4^- \rightarrow MnO_4^{--}$, while the slow, second partial reaction, $MnO_4^{--} \rightarrow MnO_2$ is not allowed to occur. The analysis of materials difficult to oxidize is thus materially shortened. With certain compounds which are easily oxidized by permanganate, the new procedure may offer an advantage if it leads to a more complete oxidation. For instance, iodide can be oxidized to periodate with the aid of the reaction: $MnO_4^- \rightarrow MnO_4^{--}$, while the older procedure with alkaline permanganate carries it only to iodate. The new method is well suited to the quantitive determination of water- or alkali-soluble organic materials. Not every carbon compound can be titrated in this way but there is no real need for this because good procedures for "wet combustion" are already available. Furthermore, the action of alkaline permanganate under the conditions described here is quite specific. It has been shown that an oxidation always begins when the molecule in question contains aliphatic carbon double bonds, or alcoholic or phenolic OH groups, or $-NH_2$, or the carbonyl group. On the other hand, an oxidation is not initiated (but also not hindered in the presence of the substituents just mentioned) by $-COOH$, $-SO_3H$, $-NO_2$, alkyl, $-Cl$, $-Br$, $-I$, and ethereal bound oxygen. The specificity makes this procedure a useful tool in the determination of constitution. In many cases the oxidative degradation of organic compounds with alkaline permanganate proceeds quantitatively to carbon dioxide and water. Consequently consumption figures are often determined which are quite advantageous for the estimation of small quantities (compare Section E). However, acetic acid, benzoic acid, and other materials which are not attacked by permanganate may appear as oxidation end products.

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[8] Sackur and Taegener, Aqueous solutions of potassium permanganate and potassium manganate. Zeit. Elektrochem. *18,* 718 (1912).

Mere reference will be made to the fact that oxidations by means of the change, $MnO_4^- \rightarrow MnO_4^{--}$ may considerably exceed in speed those carried out with bromine, iodine and other volumetric oxidizing agents.[9]

GENERAL DISCUSSION OF THE METHOD OF CARRYING OUT THE NEW PROCEDURE

To attain the highest possible oxidation velocities, the material to be determined is always added to an excess of alkaline permanganate solution. A rather high *concentration of* MnO_4^- and OH^- is chosen in order to push the equilibrium of the first stage of the permanganate reduction as far as possible to the manganate side; but on the other hand, an upper limit to these concentrations is set inasmuch as danger of loss of oxygen arises if, at times, much more free OH radical should be formed than can be consumed immediately by the material to be oxidized. It is expedient to use such quantity of alkali that the total solution at the end will be 1–2 N with respect to alkali; the permanganate should be about double that required by theory.

When deciding on the volume of the permanganate to add it should be kept in mind that the transition $MnO_4^- \rightarrow MnO_4^{--}$ furnishes only one gram-equivalent of oxygen per mole of permanganate. Under these conditions, then, a permanganate solution which is 0.1 N with respect to oxygen delivery must contain 0.1 mole of $KMnO_4$ per liter, that is, five times as much as is required for the usual 0.1 N permanganate solution. To avoid confusion, the permanganate solutions henceforth will be designated by their molarities.

The solution of the substance to be titrated should contain so much material in 10–20 cc. that of the 20 cc. of permanganate solution which is customarily exposed to reaction, at least 2 cc. and at most 10 cc. is reduced to manganate. The effect of the reading error then will not be too great, and a large excess of permanganate will be present until the end. A test titration will show whether this condition obtains. If not, another permanganate solution of more suitable molarity is substituted (for instance, 0.01 M instead of 0.1 M) or, the proper concentration of the material to be titrated is produced by diluting or concentrating its solution.

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[9] Compare Stamm, Z. angew. Chem. *47*, 794 (1934), (Hypophosphite).

In general, the quantitative oxidation of the material is complete after the reaction mixture has stood for 5–10 minutes at 15–25° C. However, with *materials difficult to oxidize,* the time may be extended to 20 minutes, or the reaction mixture may even be heated on the water bath for 5 minutes to not more than 40° C., without complications due to auto-decomposition of the permanganate.

After the oxidation is finished, the *excess of permanganate is titrated back.* This may be done *in two ways,* either in alkaline medium with formate or in acid medium with oxalic acid. The latter procedure appears simpler but is somewhat less accurate because the oxidation value of permanganate in the transition $MnO_4^- \rightarrow MnO_4^{--}$ is only one-fifth that possible in acid solution, and consequently the greater portion of the permanganate will be left over for the back-titration. The volume of the standard solution equivalent to the material being determined appears then as only a small difference between two larger values, and this is a source of error. Nevertheless, results agreeing within 0.5% may be obtained by a careful operator using good measuring equipment.

In principle, *the first procedure,* that is *titrating back* the permanganate excess *in alkaline solution,* deserves the preference. In this, the permanganate not consumed by the sample is reduced to manganate by a standard solution of sodium formate in accordance with the reaction:

$$2\,MnO_4^- + 3\,OH^- + HCO_2^- = 2\,MnO_4^{--} + CO_3^{--} + 2\,H_2O.$$

To prevent the formate from carrying the reduction of the manganate on to MnO_2, which would occur as soon as about 90% of the MnO_4^- originally present had gone over to MnO_4^{--}, a barium salt is added to the reaction mixture before beginning the addition of the formate. While barium permanganate is quite soluble in water, in conformity with the rule formulated by Weitz and Stamm[10] concerning the solubility of barium salts, barium manganate, according to Schlesinger and Siems,[11] at 25° C. has the solubility product 2.46×10^{-10}, that is, it is less soluble than barium carbonate (S.P. $= 7 \times 10^{-9}$). The MnO_4^{--} produced by the reduction consequently is bound by the Ba^{++} so rapidly that it is effectively removed from any further action of the reducing agent and the removal is so complete that, in the absence of MnO_4^- or other colored materials, the supernatant liquid is colorless. The fine pulverulent precipitate of $BaMnO_4$ is dark green, but after a little practice, it is easy to detect the color of the solution above it.

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[10] Weitz and Stamm, Monobasic, polybasic, and polymonobasic acids and their differentiation. Ber. *61,* 1148, (1928).

[11] Schlesinger and Siems, The solubility product of barium manganate and the equilibrium between MnO_4^{--} and MnO_4^-. J. Am. Chem. Soc. *46,* 1965 (1924).

A source of error in connection with the addition of the barium salt must be pointed out. If the reaction mixture contains sulfate, the barium sulfate produced will occlude significant quantities of MnO_4^- so firmly that these are removed from the reduction.[12] Consequently, *sulfate ions must be precipitated before the titration.* If the barium sulfate is not otherwise a disturbing factor it need not be filtered off, since precipitated barium sulfate will not take up MnO_4^- subsequently. If for any reason a previous precipitation of the sulfate is not possible it is better to carry out the back-titration of the excess permanganate by the second procedure (to be described).

Toward the end of the back-titration with formate the reaction velocity falls off considerably and this leads to the danger of overtitrating. In order to reach the correct end point quickly some *nickel nitrate* is now added to the reaction mixture as *catalyst.* Cobalt-, copper- or silver nitrate may be used. The acceleration is quite considerable; it apparently is the result of a process that occurs on the surface of the particles of the nickel hydroxide gel. However, if the catalyst is added too soon, it loses its activity before the end of the titration, probably because of the aging of the gel. In addition, it definitely accelerates the auto-decomposition of the permanganate as long as the MnO_4^- concentration is still high. Therefore, the nickel salt solution should be introduced only after about nine-tenths of the permanganate is already reduced.

In the *second procedure, the back-titration of the excess permanganate* is accomplished *with oxalic acid in an acid medium.* After the oxidation is finished, the mixture of permanganate, base, etc., is acidified with sulfuric acid and then decolorized with a quantity of oxalic acid equivalent to the permanganate added originally. Oxalic acid equivalent to the material being determined is left unconsumed, and is titrated with permanganate. The quantity of MnO_4^- used in this last titration is equal to that which would be used if the material being estimated permitted direct titration with permanganate in an acid medium.

In practice it is somewhat better to use the following modified procedure. A known excess of oxalic acid is used to decolorize the permanganate because it is somewhat inconvenient to invariably add the equivalent quantity of oxalic acid, whose solutions are only moderately stable. A certain portion of the permanganate consumed in the titration of the residual oxalic acid corresponds, of course, to this excess of oxalic acid, and this must be determined by a *blank,* that is, by titrating the reacting solutions against each other in the absence of the material being determined. In the actual determination, this blank is subtracted from the volume of permanganate consumed in the titration of the residual oxalic acid. The difference then represents the volume of permanganate equivalent to the material being determined.

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[12] Grimm, New types of mixed crystals, Z. Elektrochem. *30,* 467 (1924).

This second procedure is of particular importance when determining organic compounds. If these contain several carbon atoms joined to each other they produce on oxidation with alkaline permanganate not only carbonate and water but also quite often varying quantities of oxalate. The latter, after the system is acidified, will be oxidized still further. In this way many organic materials may be quantitatively converted into carbon dioxide and water. Of course, there are also numerous organic materials that produce still other oxidation products, which, like acetic and its homologues do not react further with permanganate (compare also Section B).

WORKING DIRECTIONS

PROCEDURE I: Back-Titration with Formate in Alkaline Medium

Preparation and Standardization of the Solutions. 1. 0.1 *M* Permanganate solution. The distilled water in which the permanganate is to be dissolved is boiled vigorously for five minutes in a vessel of Jena or similar glass. After adding the necessary quantity of permanganate (15.803 g. $KMnO_4$ per liter) the boiling is continued for about one minute longer. The cooling solution is allowed to stand for two hours or longer so that the MnO_2 may settle. The suspension is then filtered through a glass filter (Jena No. 4). The factor of a permanganate solution prepared in this way remains unchanged for many months. The solution is standardized against 0.5 *N* oxalic acid in the presence of sulfuric acid; 1 cc. of 0.5 *N* oxalic acid corresponds to 1 cc. of 0.1 *M* permanganate.

1a. 0.01 *M Permanganate solution.* Preparation as in 1. Standardization against 0.05 *N* oxalic acid).[13]

2. *Sodium hydroxide.* 30 g. of purest sodium hydroxide is dissolved in water and the solution made up to 100 cc.

3. *Barium chloride solution.* 30 g. of $BaCl_2.2\,H_2O$ (analytical grade) is dissolved in enough water to make 100 cc. of solution.

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[13] The statements under 1a and later in 1c and 6a refer to 0.01 *N* solutions.

4. *Nickel nitrate solution.* 1 g. of $Ni(NO_3)_2 \cdot 6\ H_2O$ (reagent grade) in 100 cc. of water.

5. *0.1 N Sodium formate solution.* 3.400 g. of HCOONa (pure, dry) and 5 g. NaOH (highest purity)—the latter stabilizes the solution—are made up to 1 liter in distilled water which has been boiled and then cooled. The solution is standardized against 0.1 *M* permanganate (solution 1) as follows:

Twenty cubic centimeters of solution 1 is pipetted into a reaction vessel (300 cc. conical flask is best), 10 cc. (graduated cylinder) of sodium hydroxide (solution 2) is added, then 15 cc. $BaCl_2$ (solution 3) and enough distilled water to bring the total volume to about 100 cc. *The red solution is titrated at room temperature with the formate solution until the color is discharged; $BaMnO_4$ precipitates. It is important when about half of the permanganate has reacted that the rest of the formate solution be added slowly (2–3 drops per second); furthermore, the solution must be thoroughly swirled during the addition of the formate. It is not necessary to wait until the precipitate has settled completely to examine the color of the supernatant liquid. It suffices to allow the solution to stand for a short time, and then tip the flask backward carefully so that a thin layer of clear solution appears at the upper edge of the liquid. This is examined against a white background. After about nine-tenths of the permanganate has been reduced, the color of the solution fades perceptibly. Then there is added 15–20 drops of nickel nitrate (solution 4) and the titration with formate is continued, with vigorous swirling, until the solution is just decolorized. If this does not occur within 2 cc. of formate after the addition of the catalyst, 5–10 drops more of nickel solution are added, since that added previously will by then have lost its activity. The nickel is added in the parallel determinations when 2–1.5 cc. less formate has been added than was found in the first titration.

The stability of the formate solution varies considerably with the purity of the constituents; it is well to determine its titer frequently, or even daily.

5a. 0.01 *N Sodium formate solution.* 0.3400 g. HCOONa and 5 g. NaOH per liter. The standardization against 0.01 *M* permanganate (1a) is carried out exactly as the standardization of solution 5; particular care must be taken to use just as much sodium hydroxide, barium chloride, water and nickel nitrate as prescribed there, not the tenth part.

Titration Procedure: Twenty cc. of 0.1 *M* (or 0.01 *M*) permanganate (solution 1 or 1a) and about 10 cc. NaOH (solution 2) are placed in the flask and into the mixture is pipetted 10 (or 20) cc. of the aqueous sulfate-free solution of the material to be determined. This mixture is allowed to stand for 10 minutes at 15–25° C.[14] About 15 cc. of $BaCl_2$ solution (solution 3) is added then and enough water to bring the total volume to about 100 cc. Then the excess permanganate is titrated back with formate (solution 5 or 5a) following the procedure just outlined for the standardization of the formate solution starting at *.

If the first titration shows that the sample has consumed more than 10 cc. of the 20 cc. of permanganate, the solutions of the sample taken for subsequent determinations must be diluted as prescribed in Section C.

PROCEDURE II: Back-Titration with Oxalic Acid in Acid Medium

Solutions. In addition to 0.1 *M* and 0.01 *M* permanganate solutions and concentrated sodium hydroxide, which are identical with the solutions 1, 1a, and 2, prescribed in Procedure I, the following will be required:

1b. 0.02 *M permanganate* containing 3.161 g. $KMnO_4$ per liter, standardized against 0.1 *N* oxalic acid.

1c. 0.002 *M permanganate solution.*

6. *Oxalic acid, somewhat* stronger than 0.5 *N*, containing about 34 g. of $H_2C_2O_4 . 2\,H_2O$ per liter; the exact strength need not be known.

6a. *Oxalic acid,* somewhat stronger than 0.05 *N*.

7. Strong *sulfuric acid* prepared by mixing 1 part by weight of pure, concentrated sulfuric acid and 1 part by weight of water.

8. *Manganous sulfate solution* containing 50 g. of $MnSO_4 . 4\,H_2O$ p liter.

Determination of the "Blank Consumption." Twenty cc. of oxalic acid (solution 6) is pipetted into the reaction vessel, treated with about 5 cc. of sulfuric acid (solution 7), and warmed to about 50° C. About 10 cc. of manganous sulfate (solution 8) is added, followed immediately by 20 cc. of permanganate (solution 1) added from a pipette. The mixture is swirled and the solution decolorizes quickly, with vigorous evolution of carbon dioxide. The excess oxalic acid is titrated then with 0.02 *M* permanganate (solution 1b); the volume of permanganate required for this is the desired "blank consumption." Since in the actual titration these same volumes of solutions 1 and 6 will be used, their titers need not be taken into account, only the "blank consumption" enters into the calculations. In the determination of this "blank" and also in the actual titration, it is very important that the solutions 1 and 6 be pipetted in exactly the same way,[15] since every error in pipetting is eventually multiplied by 5 because of the change from 0.1 *M* to 0.02 *M* permanganate in the determination of the excess. The final titration could be made with 0.1 *M* permanganate but the volume consumed would be very small and the reading error correspondingly great. The 0.02 *M* permanganate should be drawn from the burette at a rate of not more than 1–2 drops per second to exclude any drainage error.

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[14] The treatment of materials particularly hard to oxidize has been discussed on page 59.

For the dilute solutions 1a, 6a and 1c, the "blank consumption" is found by titrating a known quantity of the material to be determined; in this the experimental conditions must be kept strictly the same.

Titration Procedure. Twenty cc. of 0.1 *M* (or 0.01 *M*) permanganate (1 or 1a), about 10 cc. of sodium hydroxide (2), and 10 or 20 cc. of the solution of the material being determined are measured into the reaction vessel. The solution of the sample should conform in its concentration to the conditions stated on page 58. The mixture (normally) is allowed to stand 10 minutes (see, however, page 59). At the end of this time 10 cc. of sulfuric acid (solution 7), 20 cc. of oxalic acid (solution 6 or 6a) and about 10 cc. of manganous sulfate (solution 8) are added. The contents of the flask are swirled, the color is quickly discharged. After rapidly heating to about 50° C. the determination is completed by titrating the residual oxalic acid with 0.02 *M* (0.002 *M*) permanganate (solution 1b or 1c). This volume less the "blank consumption" gives the volume equivalent to the material being determined (compare page 60).

EXAMPLES OF THE APPLICATION OF THE METHOD

The Table on p. 65 includes some materials which are not oxidized when treated as just described. Consequently these will not interfere in titrations of mixtures containing them.

The special titration procedure for the determination of the permanganate consumption of natural waters and of sewage is described by Stamm, Z. angew. Chem. *48,* 150 (1935).

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[15] The small bore pipettes described by Ponndorf, Z. anal. Chem. *84,* 297, (1931) have proved very satisfactory.

1 Mole	Equivalents of oxygen consumed	Oxidation Products	Procedure Employed
Hypophosphite	4	Phosphate	1
Phosphite	2	Phosphate	1
Iodide	8	Periodate	1
Chloride	0	....	1
Bromide	0	....	1
Iodate	2	Periodate	1
Cyanide	2	Cyanate	1
Methanol	6	Carbonate + Water	1
Formaldehyde	4	Carbonate + Water	1
Formate	2	Carbonate + Water	1
Glycol	10	CO_2 + Water	2
Glycerine	14	CO_2 + Water	2
Erythrite	18	CO_2 + Water	2
Mannite	26	CO_2 + Water	2
Pentoses	20	CO_2 + Water	2
Hexoses	24	CO_2 + Water	2
Cane sugar*	48	CO_2 + Water	2
Maltose*	48	CO_2 + Water	2
Di-ethyl ether	0	....	1 and 2
Benzoic acid	0	....	1 and 2
Toluic acids	0	....	1 and 2
Nitrobenzoic acid	0	....	1 and 2
Iodobenzoic acid	0	....	1 and 2
Salicylic acid	28	CO_2 + Water	2
Phenol	28	CO_2 + Water	2

* Disaccharides are inverted before the determination. This is accomplished by treating the solution with 1 cc. of concentrated sulfuric acid per 50 cc. and heating in the boiling water bath for 45 minutes.

PART IV

IODATE AND BROMATE METHODS, INCLUDING MANCHOT'S BROMOMETRIC METHOD

BY

RUDOLF LANG

IODATE AND BROMATE METHODS, INCLUDING MANCHOT'S BROMOMETRIC METHOD

IODATE METHODS[1]

IODATE in acid solution is a strong oxidizing agent, whose reduction may proceed to various stages and consequently its action usually is not clear cut. However, by various means, the reduction of iodate can be forced to become unequivocal. Therefore, different types of titrations with iodate solution are possible.

METHODS BASED ON THE REDUCTION OF IODATE TO IODIDE AND FREE IODINE

The direct titration with iodate with smooth, complete reduction to iodide in accordance with the reaction:

$$IO_3^- + 6\ H^+ + 6e = I^- + 3\ H_2O \qquad (1)$$

can only be applied in exceptional cases as, for instance, to the determination of stannous chloride. The process (*1*) has attained theoretical significance as the Landolt reaction[2] but otherwise has found little practical application, because the iodate reduction very seldom proceeds quantitatively to the iodide stage.

This reduction of iodate may serve as a basis for calculation if the material being determined is oxidized at room temperature with excess iodate, and this excess, together with the reduction products (mostly free iodine), is treated with potassium iodide, and then titrated with thiosulfate solution. If the oxidation with excess iodate is carried out in a sulfuric acid solution containing no nitrate or chloride, and if the liberated iodine is volatilized by boiling, the oxidizing action of the iodate may be represented:

$$2\ IO_3^- + 12\ H^+ + 10\ e = I_2 + 6\ H_2O \qquad (2)$$

assuming, as Rupp (13) emphasized, that no disturbing side- or subsequent reactions occur.

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[1] This chapter will touch also on certain periodate methods.

[2] Landolt, Ber. *19*, 1317 (1886); Eggert and Scharnow, Ber. *54*, 2521 (1921); Z. Elektrochem. *27*, 455 (1921); Skrabal, Z. Elektrochem. *28*, 224 (1922); Thiel and Meyer, Z. anorg. allgem. Chem. *137*, 125 (1924).

Under certain circumstances the measurement of the excess iodate, according to Schwicker (65), can be made in the absence of iodide, by means of a bisulfite solution stabilized with ethyl alcohol. The applicability of this type of procedure depends on the condition that the oxidation product is not again reduced by iodide, and consequently its use is limited.

METHODS BASED ON THE REDUCTION OF IODATE TO POSITIVE UNIVALENT IODINE

Procedures that are generally applicable are reached if the reaction conditions are so chosen that the iodate can react farther with its reaction products, namely iodine or iodide, to form positive univalent iodine quantitatively. Methods based on this were proposed by Andrews (8, 9) by the writer (34, 47, 88), and by Berg (51).

The reactions which serve as a common basis for all these procedures are most simply explained and formulated as follows:

The non-polar iodine molecule under the influence of polar solvents, such as water, becomes a dipole. For this reason, probably, iodine dissociates to a slight extent in such solvents, as indicated by the equation:

$$I_2 \rightleftharpoons I^+ + I^- \qquad (3)$$

A reduction of iodate in accordance with equation (*2*) by the material being titrated is therefore, at first, connected with the establishment of equilibrium (*3*). On further action of the iodate, I^- is directly changed into I^+:

$$2\,I^- + IO_3^- + 6\,H^+ = 3\,I^+ + 3\,H_2O \qquad (4)$$

Because equilibrium (*3*) persists, this change in charge results in the quantitative oxidation of the free iodine to I^+. The summation of (*2*), (*3*), and (*4*) leads to the following representation of the oxidation of iodine:

$$2\,I_2 + IO_3^- + 6\,H^+ = 5\,I^+ + 3\,H_2O \qquad (5)$$

The end of the titration is reached through this reaction, whose completion is shown, in the presence of a suitable indicator, by the disappearance of the free iodine. The same successive reactions occur if iodate is first wholly or partially reduced according to (*1*). Consequently, in such titrations, the total reduction of iodate is always determined by the reaction:

$$IO_3^- + 6\,H^+ + 4\,e = I^+ + 3\,H_2O \qquad (6)$$

The reaction scheme just given describes, in simplest form, merely the stoichiometric relationships without, however, giving any information about the further behavior of the cation I^+, which probably is stable only in the slightest concentration. In all titration methods of this kind, the I^+ primarily formed changes at once into stable compounds of positive univalent iodine. Depending on the conditions, the titration gives *iodine monochloride, iodine bromide, iodine cyanide,* or *iodo-acetone* as the end product of the iodate reduction.

The choice of the indicator depends on the state of equilibrium (*3*) near the end of the titration. In the central state starch is quite suitable, whereas quite far toward the right or left, only chloroform or carbon tetrachloride will indicate the presence of free iodine with sufficient certainty.

In certain titrations, and also in the determination of small quantities of materials, reaction (*5*) sometimes proceeds more quickly than the oxidation of the material being determined; then, after the end point has apparently been reached iodine appears repeatedly. Under some conditions, the primary reduction of the iodate will not go beyond the stage $I(+1)$, and free iodine does not separate at all. In these cases, the direct titration can usually be made possible by a preliminary oxidation with iodine monochloride, iodine cyanide, or hypoiodous acid. In the pre-oxidation a quantity of free iodine equivalent to the material being determined is produced according to the equation:

$$2\ I^+ + 2\ e = I_2$$

and this then may be titrated with iodate. In many cases the pre-oxidation can be accelerated by using a cupric or ferric salt as catalyst (compare p. 94, Determination of Ti, V, Mo, W, U). In certain cases instead of pre-oxidizing and then titrating, the oxidation may be accomplished with excess iodate and the excess then titrated back with arsenious acid to the stage $I(+1)$. If the delay in the separation of iodine is due to the energy relationships rather than to the kinetics of the system, iodate methods cannot be used.

THE ANDREWS METHOD (8, 9, 54)

The Iodine Monochloride Procedure. Andrews' original method, the oldest procedure of this kind, is characterized by the production of positive univalent iodine as iodine monochloride under the prescribed conditions, namely titration in strong hydrochloric acid solution.

Positive univalent iodine in concentrated hydrochloric acid probably forms complex ions. Philbrick[3] postulates the formation of the ion ICl_2^-:

$$I^+ + 2\,Cl^- \rightleftharpoons ICl_2^- \qquad (7)$$

Accordingly equilibrium (*3*) will take the form:

$$I_2 + 2\,Cl^- \rightleftharpoons ICl_2^- + I^- \qquad (8)$$

Since it is shifted quite in favor of free iodine, chloroform or carbon tetrachloride may serve as indicator in the Andrews method, but starch can not be used.

If the hydrochloric acid concentration is too low, equilibrium (*7*) produces I^+ cations in greater measure and these then undergo hydrolysis:

$$I^+ + H^{(+)}OH^{(-)} \rightleftharpoons HOI + H^+ \qquad (9)$$

This reaction must not attain any considerable proportions during the titration, because the hypoiodous acid formed undergoes the following reaction:

$$5\,HOI \rightleftharpoons 2\,I_2 + IO_3^- + H^+ + 2\,H_2O \qquad (10)$$

and thereby brings about an overconsumption of iodate. The hydrolysis of iodine monochloride is avoided if the content of concentrated hydrochloric acid is kept above 33% by volume.

Experiments by the writer (88) have shown that a deficiency of hydrochloric acid, provided its concentration does not fall below 10% by volume, may be replaced almost completely in its inhibiting effect on the hydrolysis by potassium chloride, with which the solution should be saturated.

The writer's experience has demonstrated that the following *general procedure* can be used as a guide for titrations of this kind: The reaction is carried out in a flask with a perfectly-fitting stopper. A measuring flask with a short neck is best. The solution (at least 50 cc.) of the sample is treated with an equal volume of concentrated hydrochloric acid (sp. gr. 1.19) and 5 cc. of carbon tetrachloride. After cooling to room temperature the solution is titrated with 1/40 or 1/60 *M* potassium iodate solution, with vigorous shaking, until the last drop decolorizes the layer of indicator that collects in the neck of the inverted flask. Near the end of the titration the flask must be closed and thoroughly shaken after the addition of each drop of iodate solution.

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[3] Philbrick, J. Am. Chem. Soc. *56*, 1257 (1934). The early literature is given in Gmelin, "Handbuch der anorganischen Chemie," 8th Edition. System No. 8, p. 627 (1933).

Small quantities of material, with the exception of iodide and iodine, are oxidized before the titration by adding iodine monochloride solution. This must be done, if possible, at a low acidity, because the HOI formed by hydrolysis at low concentrations of hydrochloric acid has a much quicker oxidizing action than the ion ICl_2^-.

Most of the heavy metals do not affect the reaction. Silver salts interfere only if so little hydrochloric acid is used that silver salt remains dissolved to the end of the titration. The effect of bromide is discussed under "The Iodine Bromide Procedure."

Use of Other Standard Solutions

In the titration of iodide, iodate solution may be replaced by solutions of other strong oxidizing agents (2, 3, 41, 48, 61, 69, 70, 72, 74, 80, 83, 98) also in the determination of other materials which have been pre-oxidized with ICl (62, 71, 80, 91). According to Swift (70) titrations of iodide with bichromate require an end concentration of at least 66% by volume of hydrochloric acid, otherwise the reaction velocity is too low. When working with quick acting oxidants such as permanganate or ceric sulfate, a concentration of at least 33% by volume of hydrochloric acid must be maintained to avoid the error arising from hydrolysis.

The Iodine Bromide Procedure. Iodine bromide is the end product of the reduction of iodate if bromide is present in the Andrews titration. Andrews (8, 9) thought that his method was not applicable in the presence of bromides. On the other hand, several writers have found that titrations, particularly of iodide, are feasible in the presence of smaller (52, 57, 69, 72, 77, 98) and larger (74, 81, 83, 90, 141, 142, 152) quantities of bromide, using iodate and other oxidizing agents in the presence of carbon tetrachloride as indicator. Or a potentiometric ind cation may be used. Winkler and v. Vegh (142) were the first to establ the favorable effect of quite large quantities of bromide. Mutschin (9 increased the bromide concentration until the solution was saturat with KBr. In order to clear up several points the writer (88) studie the effect of the bromide concentration and offers the following explanation of its action.

In contrast to iodine monochloride, iodine bromide partially dissociates into its elements, so that in aqueous solution:

$$2\ I^+ + 2\ Br^- \rightleftharpoons I_2 + Br_2 \qquad (11)$$

and chloroform and carbon tetrachloride are colored violet to pink by iodine bromide. Therefore, in the presence of bromides Andrews titrations are only possible if the iodine bromide does not split into its elements. This is the case under certain conditions as may be seen in Figure 1.

The area to the left of the curve represents those final concentrations of I (+ 1) and of Br^- at which the Andrews method can be carried out. The curve is not to be regarded as a sharp boundary but rather as representing an indefinite transition zone which leads to that concentration range within which the indicator remains distinctly pink, both at the equivalence point and beyond. In general, there are for higher iodine concentrations two limits of permissible bromide concentration, a lower one to be kept within, and a higher one which may be exceeded at will.

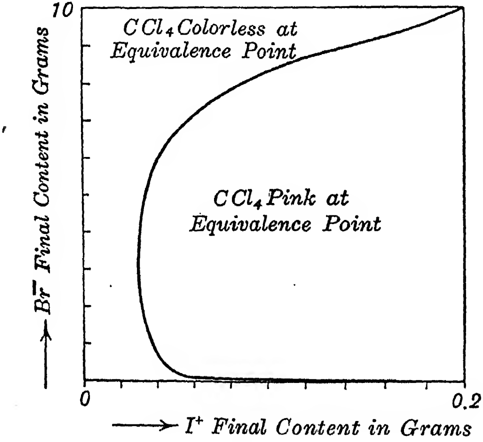

Fig. 1

Iodide titrated with iodate in presence of bromide. Final volume: 100 cc. Final acid content: 35 vol. % HCl (sp. gr. 1.19). Indicator: 5 cc. CCl_4.

In the first case equilibrium (*11*) lies far to the left because of too low bromide ion concentration. In the second case the I^+ ion goes over into a complex IBr_2^- which is not appreciably dissociated:

$$I^+ + 2\ Br^- \rightleftarrows IBr_2^-$$

Reaction (*11*) is then forced to completion toward the left. As the quantity of iodine diminishes, the limits of the permissible bromide concentrations approach each other and finally merge when the iodine concentration is correspondingly low. If not more than about 30 mg. of iodine is present per 100 cc. final volume, the bromide concentration is optional.

The iodine bromide procedure, in the narrower sense, consists of titrations at higher bromide concentrations, at least 1.3 molar. In contrast to the iodine monochloride procedure it may be carried out at acidities, for example with a hydrochloric acid content of 0.5% by volume (88). Complex iodine bromide is not markedly hydrolysed so long as the solution is still distinctly acid. It furnishes to too small an extent iodine cations which would undergo hydrolysis and disproportionation.[4] A lower limit to the acidity is only drawn because the reaction velocity becomes too small.

The following *directions* may be taken as a general guide for titrations by the iodine bromide procedure:

1. For titrations of iodide iodine or free iodine up to a maximum of 160 mg. The sample, in a 300 cc. measuring flask, is treated with a concentrated solution of 22 g. of KBr.[5] Five cc. of concentrated hydrochloric acid is added, the solution diluted to 100 cc., 5 cc. of carbon tetrachloride introduced, and then the titration with iodate solution is accomplished, with thorough shaking of the sample. The decolorization of the carbon tetrachloride layer can be observed perfectly only when the closed flask is inverted. Other materials are determined in this manner, provided they do not consume more than 50 cc. of 1/40 *M* iodate solution. In case they require pre-oxidation a maximum of 2.5 cc. of 0.5 *M* iodine monochloride solution may be used.

2. For titrations of solutions containing up to 310 mg. of iodine. The sample is treated with a concentrated solution of 37 g. of KBr and 5 cc. of concentrated hydrochloric acid, the solution is diluted then to 200 cc. and titrated after the addition of carbon tetrachloride. Up to 5 cc. of 0.5 *M* iodine monochloride solution may be used for the pre-oxidation of iodine-free materials.

USE OF OTHER STANDARD SOLUTIONS

In the iodine bromide procedure also, other oxidizing agents may be used in place of iodate (74, 81, 83, 88, 141, 142, 152).[6] The writer (88) has found that the titration of iodide with 0.1 *N* bichromate solution requires, at the end point, a minimum acidity of 30% by volume of concentrated hydrochloric acid. In the presence of as little as 5% by volume of concentrated hydrochloric acid, iodide can be smoothly titrated with 0.1 *N* solutions of periodate, permanganate, bromate, ceric sulfate, bromine or chloramine-T. This acidity is not the lower limit; for several of these oxidizing agents, such as permanganate or bromine, it is just as low as for iodate.

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[4] The transformation of a substance into two dissimilar compounds by a process involving simultaneous oxidation and reduction.

[5] The bromide must be free from iodide, iodate, and bromate. However, bromide not meeting these specifications can be used. In this latter case, 0.5–1 cc. of 0.05 *M* iodide solution is titrated in the presence of 22 or 37 g. of the bromide plus some acid, and then the whole is added to the solution of the sample, which may be titrated then.

[6] See also Winkler, "Ausgewählte Untersuchungsverfahren für das chemische Laboratorium." New Series, p. 100 (1936).

PRE-OXIDATION WITH ALKALINE IODINE-HALIDE SOLUTION

Certain compounds that do not react in acid solution with iodate are made accessible to titration with this reagent if they are subjected to a pre-oxidation with hypoiodite solution. This is particularly true of organic materials. The hypoiodite is made by adding alkali to an iodine halide. Iodine monochloride, with which a large excess of potassium bromide has been mixed, is especially suitable for pre-oxidation in alkaline solution, since after being made alkaline it changes its oxidizing value through loss of oxygen much less readily than a bromide-free alkaline solution, which quickly loses its activity (88).

Following the pre-oxidation and acidification with hydrochloric acid the titration can be carried out by the iodine bromide method. The determination of formaldehyde (p. 98) is an example.

LANG'S IODINE CYANIDE METHOD (34, 47)

This method, which Kolthoff termed the iodine-cyanide method, is based on titration with iodate in the presence of hydrogen cyanide, the iodate being quantitatively converted into iodine cyanide.

The cation I^+ reacts with hydrogen cyanide:

$$I^+ + HCN = ICN + H^+ \qquad (12)$$

The summation of (*12*), or multiples of it, and (*3*) to (*6*) gives the reaction scheme for this procedure. (*3*) plus (*12*) gives the equilibrium:

$$I_2 + HCN \rightleftarrows ICN + I^- + H^+. \qquad (13)$$

The favorable state of this equilibrium permits the use of starch as indicator. According to Kovach[7] $\frac{[HCN]\,.\,[I_2]}{[ICN]\,.\,[I^-]\,.\,[H^+]} = 1.37$ at 25° C.

At the end of the titration the concentrations $[I_2]$ and $[I^-]$ simultaneously approach the value = 0 and consequently the solution becomes colorless.

Titrations in the presence of hydrogen cyanide require a H^+ concentration of not less than 1 *N*. This acidity suffices for iodate to immediately oxidize I^- in highest dilution, either in 1 *N* hydrochloric or in 2 *N* sulfuric acid, provided the solution contains a little chloride. The oxidation proceeds more slowly in the absence of chloride ion which acts catalytically. The titrations may also be made in solutions containing only sulfuric acid but the procedure is correspondingly slow. Hydrolysis of the positive univalent iodine is not involved in this method because iodine cyanide, which dissociates practically not at all, is decomposed hydrolytically at room temperature only in alkaline solution.

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[7] Kovach, Z. phys. Chem. *80*, 107 (1912).

If the titrations are made in the presence of hydrochloric acid, there appears as an intermediate product iodine monochloride which, depending on the concentration of the hydrogen cyanide and hydrochloric acid, goes over, more or less quickly, into iodine cyanide. The iodine-starch reaction functions precisely only after this transition is quantitatively complete. Therefore, the $\frac{HCN}{HCl}$ must be controlled in the titration. If the starch-iodine reaction recurs too slowly toward the end of the titration because the hydrochloric acid concentration is too high, the solution must either be diluted with water, or neutralized with ammonia, or more potassium cyanide must be added. A high concentration of sulfuric acid is not detrimental to the indicator action of the starch, unless the chloride concentration is too high.[8]

The method can be used also in the presence of considerable quantities of bromide. If the titration is carried out by running practically the whole quantity of iodate in at one time, excellent results are still obtained, provided the hydrochloric acid solution contains not much more than 1 g. of KBr per 100 cc. If the standard solution is added drop by drop throughout the titration this limiting concentration is considerably higher. Experience has shown that the permissible bromide concentration is lower in sulfuric acid solution. Toward the end of the titration bromides cause a color change after each drop from red-brown through violet to blue. To obtain a sharp end point it is necessary to delay each further addition until the solution turns violet at least.

The method may be used also as a bromometric procedure, either to accomplish a rapid oxidation, or to carry out a bromination. The active agent here is the bromine liberated from potassium bromide in hydrochloric acid solution by the excess iodate:

$$IO_3^- + 5\ Br^- + 6\ H^+ = IBr + 2\ Br_2 + 3\ H_2O.$$

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[8] See Lang, [(34) (47 II)] concerning the reactions of hydrogen cyanide on iodine monochloride, iodine bromide, hypoiodous and hypotri-iodous acids.

The excess is titrated back with arsenious acid or hydrazine sulfate:

$$IBr + 2\ Br_2 + 2\ As^{+++} + HCN = ICN + 5Br^- + As^{+++++} + H^+$$

At the end of the titration then the total iodate iodine reappears as iodine cyanide.

In addition to titration in the presence of moderate quantities of bromide, the cyanide procedure is eminently suited for the analysis of mixtures of certain materials, that is, substances which behave differently according to whether the solution titrated contains hydrochloric acid, sulfuric acid or bromide. The method can not be used if silver or mercury salts are present, because they precipitate or combine with I^-. The determination of quite a number of substances in the presence of each other can be accomplished if the iodine cyanide produced by the titration with iodate is then titrated with thiosulfate. According to Meinecke[9] the reaction between these materials proceeds smoothly in acid medium:

$$ICN + 2\ S_2O_3^{--} + H^+ = I^- + HCN + S_4O_6^{--}.$$

Throughout this reaction, in accordance with equilibrium $(\underset{\leftarrow}{13})$, there is produced free iodine whose disappearance marks the end of the titration. There is no need to add potassium iodide in this titration.

The directions for direct titrations by the cyanide procedure follow: The approximately neutral solution of the sample, in a long narrow-necked flask (a volumetric flask, for instance), is acidified with its own volume or, in any case, with at least 50 cc. of 2.5 N HCl. Then 6–8 cc. of 0.5 N KCN and some starch solution are introduced and the titration with 1/40 or 1/60 M KIO_3 solution is carried to the discharge of the blue coloration, which appears at the beginning of the titration. Instead of acidifying with hydrochloric acid, enough sulfuric acid may be substituted to bring the concentration up to 2 N, adding 1–2 g. of NaCl per 100 cc. volume.

Small quantities of materials (iodide and iodine excepted) which will probably consume less than 3 cc. of 1/40 M iodate solution are oxidized with several drops or even several cc. of iodine chloride solution before the titration. After this pre-oxidation an adequate excess of potassium cyanide must be added. For x cc. of 0.5 M iodine monochloride solution, $x + 6$ cc. of 0.5 M potassium cyanide solution suffices. Iodine cyanide may also be used as pre-oxidant; it is simpler to use the solid preparation. In this case about 5 cc. of 0.5 M potassium cyanide solution must be added before the titration.

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[9] Meinecke, Z. anorg. allgem. Chem. *2*, 157 (1892).

The bromometric procedure and the titration of the excess are carried out as follows: About 30 cc. of the approximately neutral solution of the sample is treated in a measuring flask with 1 g. of KBr and 20 cc. of 1:1 HCl. Excess (up to about 45 cc.) of 1/40 *M* iodate solution is added from a burette. After sufficient delay, which should be kept constant for each case, starch is introduced and the titration made with 0.1 *N* arsenious acid solution, added in portions of 0.5–1 cc. until the solution is permanently dark brown. Then 8 cc. of 0.5 *N* potassium cyanide is added and after waiting until the blue color appears the titration with the iodide is carried to a sharp end point. A customary titration of the excess is carried out in the same manner, without the addition of any bromide.

USE OF OTHER STANDARD SOLUTIONS

In the presence of hydrogen cyanide other oxidants may, under the following conditions, be substituted for iodate in the determination of iodide or other materials previously oxidized with iodine monochloride or iodine cyanide: (a) *Periodate* [(34) 47 IV]. The titration is carried out as with iodate but always in the presence of 0.5–1 g. of potassium bromide per 100 cc. Cf. p. 86. (b) *Permanganate* (1, 34, 37, 43, 46, 50). The titration is carried to a pink in 1 *N* HCl or 2 *N* H_2SO_4 solution, or to colorless in hydrochloric acid solution in the presence of starch. These titrations must be accomplished by adding the permanganate drop by drop and with constant swirling of the solution containing the sample. A local excess of permanganate may lead to the formation of chlorcyanogen in hydrochloric acid, or of iodate in sulfuric acid solution, and so bring about over-consumptions. Bromide must not be present. (c) *Ceric sulfate.* The titration is made, according to Someya (66), potentiometrically or, according to the writer's experience, in 1 *N* HCl with ferroïn as indicator. Any turbidity will disappear toward the end of the titration. Bromide up to 1 g. of KBr per 100 cc. does not interfere. The iodine-starch end point is not sharp enough in the titration with ceric salt. (d) *Chloramine-T.* According to Berry (80) the titrations this material are like those with iodate. (e) *Bromate.* (125). See

BERG'S IODO-ACETONE METHOD (51)

In this method the titration with iodate is made in the presence *acetone,* whose function is similar to that of hydrogen cyanide.

Acetone reacts with the cation I^+:

$$I^+ + C_3H_6O = C_3H_5OI + H^+$$

(It is arbitrarily assumed here that only monoiodo-acetone is formed.) The sum of (*3*) + (*14*) gives an equilibrium analogous to (*13*):

$$I_2 + C_3H_6O \rightleftarrows C_3H_5OI + H^+ + I^- \qquad (15)$$

Under the conditions prescribed in this method, the equilibrium is shifted so far toward the right that starch no longer reveals the presence of free iodine, even when the titration is far from completion. The titration is made in 1 *N* hydrochloric or 2 *N* sulfuric acid solution, with the addition of 20–30 cc. of acetone per 100 cc. volume.

The course of the titration (unpublished studies by the writer) with *starch* as indicator is as follows: Every drop of the iodate solution produces an intermediate blue coloration that always disappears after a short time. The end of the titration is reached when the last drop no longer produces a transient blue. Only in the titration of larger quantities of iodide does a permanent blue appear at the beginning, but as the iodide is consumed the coloration becomes fleeting. The continual disappearance of the blue makes the detection of the end point difficult and the uncertainty grows with increasing volume. Variation of the acid and acetone concentrations never produces so favorable a shift in the equilibrium that free iodine is permanently revealed by starch throughout the whole titration as in the cyanide procedure.

If the more sensitive chloroform is used as indicator in Berg's method, free iodine may be detected at any stage of the titration, but it should be noted that in the presence of acetone the solution of iodine in chloroform is not violet but brown. Just before the end point is reached the chloroform is slightly yellow and this color disappears on the addition of the last drop of iodate.

Berg used his method only for the determination of iodides. However, if the volume is kept small the method may be employed for the titration of arsenious acid and in all probability for still other materials (the writer's unpublished results).

See (89) concerning the use of ceric sulfate in place of iodate for the determination of iodides by the acetone method.

As to the *accuracy* of the various methods based on the production of positive univalent iodine it may be said, assuming the purity of the reagents, that in general if the prescribed conditions are maintained the results will correspond to the theoretical ones. This means that the methodical error is considerably smaller than the sum of the general titration errors, which therefore predominantly affect the accuracy of the determination.

In attempts to attain the greatest possible accuracy in titrations with very dilute iodate solutions the following facts must be taken into account: *Direct titrations with 1/600 M iodate solution must always be preceded by oxidation with iodine monochloride solution (except in the determination of iodine or iodide) so that the iodine will be increased to the point where the end of the titration can be sharply distinguished.* This applies to Andrews' method as well as to the cyanide procedure. As to the latter it must be noted further that, with reference to the position of equilibrium (*13*), the cyanide excess must not be too great. According to Kolthoff (45) in titrating with 1/600 *M* iodate solution the iodine-starch end point can still be detected if the cyanide solution is even ten times as dilute as in the ordinary titration. Because of the uncertain end point the acetone procedure should not be attempted with iodate solutions which are more dilute than about 1/60 *M*. All the difficulties in detecting the end point in the titration with very dilute iodate solutions are obviated if the potentiometric indication is used.

Kolthoff (45) has made observations on the accuracy of *micro-titrations* with iodate. He found that 0.1 mg. of iodine in 100 cc. of solution can be determined with an accuracy of 1% by titration with 1/60,000 *M* iodate solution by the cyanide method, using carbon tetrachloride as the indicator. It is very likely that approximately the same degree of accuracy may be reached in the micro-titration of other materials if they are subjected to pre-oxidation with iodine monochloride.

Titrations in the Presence of Mercuric Salt. Recently Hovorka (73, 75) and then particularly Furman and his collaborators have worked out titration methods using iodate in the presence of mercuric salt. The latter authors found that materials that otherwise reduce iodate in accordance with equation (*2*) can, in the presence of mercuric salt, be titrated directly with reduction of the iodate according to equation (*1*). Among such materials are, according to Schoonover and Furman (79), trivalent arsenic, and according to Miller and Furman (private communication to the editor), trivalent antimony, hydrazine and its derivatives such as phenylhydrazine, semicarbazide, etc.

The action of mercuric salt is due to the shifting of equilibrium (*3*) toward the right as a consequence of binding I^- into complexes. Because of the simultaneous rise of I^+ concentration such a powerful and rapid oxidizing action is obtained that the free iodine is reduced immediately and quantitatively to the iodide stage. According to Miller and Furman the potential $I_3^-/3\ I^-$, in solutions that are 1–3 *N* with respect to hydrochloric acid and contain 15–30 cc. of saturated mercuric chloride solution per 100 cc., becomes 0.2–0.3 volt more noble than in the absence of the mercuric salt. Its action decreases with increasing concentration of hydrochloric acid, for then binding of the I^- is looser, and besides the oxidizing effects of the I^+ are retarded because of the formation of the ICl_2^- complex.

The best hydrochloric acid concentration for this type of titration is about 0.5–2 *N* when 15–30 cc. of saturated mercuric chloride solution is used per 100 cc. The end point is determined potentiometrically or with the aid of carbon tetrachloride.

After titrating to the iodide end point and then raising the hydrochloric acid concentration to 4–6 *N*, the titration can be continued to the ICl end point. The second titration is particularly advantageous if iodide is to be determined in addition to one of the materials mentioned before. In this case the iodate consumed in the second titration less half that consumed in the first titration, corresponds to the iodide being determined. Thus both materials can be determined in a single operation. According to Miller and Furman, the titration to the iodide end point under the same conditions can be accomplished with an iodine solution also (private communication to the editor).

PARTICULAR DETERMINATIONS

The requisite solutions are:

Potassium Iodate. 1/40 or 1/60 *M*. 5.3492 or 3.5661 g. of KIO_3 (recrystallized twice and dried at about 150° C.) per liter.

Arsenious Acid. 0.1 *N*. About 5 g. of As_2O_3 is dissolved by warming in sodium carbonate solution containing about 2.5 g. of Na_2CO_3, and diluted to 1 liter. It is standardized against the iodate solution.

Iodine Monochloride. 0.5 liter of roughly 0.5 *M* ICl solution is prepared by dissolving 17.5 g. of KIO_3 and 27.7 g. of KI in 250 cc. of water, transferring the solution to a 1 liter volumetric flask, adding 200 cc. of concentrated hydrochloric acid, followed by 10 cc. of chloroform. The cooled contents of the flask are titrated with 1/40 *M* iodate solution by the Andrews method. In the titration of this large volume long and vigorous stirring is essential to the establishment of the equilibrium each time. It is better in this preparation to use a potentiometric indication rather than chloroform. The iodine monochloride solution must be stored in the dark.

Potassium Cyanide. An approximately 0.5 *M* solution is prepared by dissolving 33 g. of the commercially pure salt per liter. Twenty cc. of this solution, when treated with 2 g. of KI, 30 cc. of 1/40 *M* iodate solution and 100 cc. of normal hydrochloric acid, should, when titrated with 0.1 *N* $Na_2S_2O_3$ solution, consume the same volume as does this mixture without the cyanide solution. Furthermore, 20 cc. of the cyanide solution when acidified with sulfuric acid should give a permanent pink on the addition of 1 drop of 0.1 *N* permanganate solution. Commercial potassium cyanide sometimes varies considerably in this respect and must always be tested.

In the following, the iodine monochloride procedure will be referred to as Method A_1*, the iodine bromide procedure as* A_2*, the cyanide procedure as B, and the acetone procedure as C.*

Iodide and Iodine. Alkali iodide and elementary iodine can be titrated by Methods A_1, A_2, B and C. One cc. of 1/40 *M* KIO_3 corresponds to $\frac{126.91}{2 \times 10^4}$ g. of iodide iodine and to $\frac{126.91}{10^4}$ g. of free iodine. Method A_2 is best when any considerable quantity of bromide is present. Mutschin (90) has used it to determine iodide in the presence of 200 g. of KBr. In the presence of bromide up to 1 g. of KBr per 100 cc., B and C can be used conveniently (34, 51). Method C permits the subsequent determination of bromide and chloride argentometrically. The micro-determination of iodide is discussed in (45, 74, 81, 141, 152).

Two Oxidation Stages of Iodine (34). (a) *Iodine plus iodide.* First iodine and iodide are titrated together by Method B, and then the iodine cyanide formed is titrated with thiosulfate. If i cc. of 1/40 *M* KIO_3 and t cc. of 0.1 *N* $Na_2S_2O_3$, standardized against the iodate solution, have been consumed, then

$$(2.5\,i - t)\,\frac{126.91}{2 \times 10^4} \text{ g. of iodide iodine and}$$

$$(t - 1.5\,i)\,\frac{126.91}{10^4} \text{ g. of free iodine were present.}$$

(b) *Free iodine plus univalent positive iodine.* The procedure is the same as in (a). The free iodine is equal to $i\,\frac{126.91}{10^4}$ g., the univalent positive iodine to $(t - 2.5\,i)\frac{126.91}{2 \times 10^4}$ g. (c) *Iodine plus iodate.* First the iodine and iodate are titrated together with bisulfite or stannous chloride in about 1 N hydrochloric acid solution, until the iodine-starch color, which appears in the course of the titration, is just discharged. The iodide formed is then titrated immediately by Method B. If s cc. of 0.1 N bisulfite or stannous chloride solution and i cc. of 1/40 M iodate solution are used, then $(3\,i - s)\frac{126.91}{5 \times 10^4}$ g. of free iodine, and $(2\,s - i)\frac{126.91}{10^5}$ g. of iodate iodine were present. The bisulfite or the stannous chloride solution should be standardized against the iodate solution at the time of the determination.

Difficultly Soluble Iodides (47 II). (a) *Cuprous Iodide.* About 0.3 g. of the salt is dissolved in 10 cc. of 0.5 M KCN solution, the solution acidified with 20 cc. of 1 : 1 HCl, diluted to 100 cc. and titrated with iodate in the presence of starch. The cuprous salt is oxidized to cupric salt and the iodide to ICN. After adding 12 g. of dissolved ammonium oxalate and 2 g. of potassium iodide, the system is titrated with thiosulfate which gives a measure of the ICN alone. The iodine cyanide arising from the iodate must be taken into account and accordingly one-half of the volume of the 1/40 M iodate solution consumed should be subtracted from the thiosulfate consumption. One cc. of 0.1 N $Na_2S_2O_3$ then corresponds to $\frac{126.91}{2 \times 10^4}$ g. of iodide iodine. (b) *Lead iodide.* Up to 0.4 g. of the salt is dissolved in a little base, treated with 5 cc. of ICl, 20 cc. of 1 : 1 HCl, 10–15 cc. of KCN, and then titrated with iodate in the presence of starch. (c) *Mercuric iodide.* Up to 0.45 g. of the salt is dissolved in 100 cc. of 1 : 1 hydrochloric acid, and titrated by Method A_1. (d) *Silver iodide.* Up to 0.45 g. of the salt is dissolved in 10 cc. of KCN solution, and reduced at the boiling point, with granulated iron-free zinc, a little base being added. The progress of the reduction to metallic silver can be followed by acidifying small test portions. If silver iodide still precipitates, the test portion is again made alkaline and returned to the main solution. After the reduction is complete, the suspension is filtered, the precipitate washed (first with water, then with dilute hydrochloric acid), the filtrate is acidified with about 12 cc. of concentrated hydrochloric acid and titrated with iodate after the addition of starch. Unpublished studies of the author have shown that silver iodide may also be dissolved in the smallest possible volume of potassium cyanide solution, strongly acidified with hydrochloric acid and then titrated by Method A_1. Toward the end of the titration about 75% of concentrated hydrochloric acid should be present to keep the silver salt in solution.

Iodide and Bromide in the Presence of Each Other. These materials may be determined, one after the other, by Method B [(47) IV, p. 79]. For practical purposes, especially in the presence of considerable quantities of chloride, the thiosulfate methods of the writer are somewhat better. Details are given in [(47) IV, p. 80]. See also (68).

Cyanide [(47) III] can be determined by the bromometric Method B. The solution is allowed to stand closed for 1 minute before the back-titration of the iodate. According to the reaction equation:

$$2\,HCN + IO_3^- + 3\,Br^- + 4\,H^+ = 2\,BrCN + IBr + 3\,H_2O \qquad (16)$$

1 cc. of 1/40 *M* iodate solution corresponds to $\frac{13}{10^4}$ g. of cyanogen (CN). The determination of iodide and cyanide in the presence of each other may be accomplished by titration with iodate (47 III p. 288).

Thiocyanate [(47) III]. The oxygen of the air takes part in the oxidation of thiocyanate by iodate in moderately strong hydrochloric acid solution and this participation is greater the slower the titration and the smaller the quantity of thiocyanate present. If the titration is carried out with sufficient speed this extraneous oxidation is negligible. The following methods, employing an excess of the oxidant, are reliable. The solution of the alkali thiocyanate, which should be about 1.5 *N* with respect to HCl, is treated with an excess of iodate solution added rapidly from a burette. Then the mixture is swirled for the first time, and titrated back with arsenious acid, either according to Method B or, after the addition of potassium iodide, with thiosulfate. The bromometric Method B is also applicable if the directions given on p. 79 are modified as follows: The neutral thiocyanate solution containing 1 g. of KBr is first treated with iodate and only then acidified with 30 cc. of 1:1 HCl, the flask is closed tightly and the back-titration with arsenious acid is begun after 2–3 minutes. This procedure prevents, during the bromination, the formation of iodine cyanide which is no longer susceptible to bromination.

The direct titration of thiocyanate by Method A_1 proceeds without any interference by atmospheric oxygen. A direct titration can also be carried out according to Method B, the action of the air being definitely eliminated by a pre-oxidation with iodine monochloride or iodine cyanide.

The following equations give the basis for the calculation:

1. *Excess Titrated with Thiosulfate.*

$$CNS^- + IO_3^- + H_2O = SO_4^{--} + HCN + I^- + H^+ \qquad (17)$$

2. *Methods A and B.*

$$2\,CNS + 3\,IO_3^- + HCN + H^+ = 2\,SO_4^{--} + 3\,ICN + H_2O \qquad (18)$$

3. *Bromometric Method B.*

$$CNS^- + 2\,IO_3 + 3\,Br^- + 4\,H^+ = SO_4^{--} + BrCN + 2\,IBr + 2\,H_2O \qquad (19)$$

Consequently, 1 cc. of 1/40 M iodate solution corresponds to:

1. $\frac{58.05}{4 \times 10^4}$ g., 2. $\frac{58.05}{6 \times 10^4}$ g., 3. $\frac{58.05}{8 \times 10^4}$ g. of thiocyanate (CNS).

Thiocyanate and Iodide Together [(47) III]. The total of both of these materials is titrated first by the direct Method B without pre-oxidation. In this joint titration atmospheric oxygen does not participate in the oxidation of the thiocyanate, even when the titration is made slowly, provided the quantity of iodide present is not too small. The titration with iodate is followed immediately by one with thiosulfate, whereby the total iodine cyanide formed is measured. If i cc. of 1/40 M KIO_3 solution and t cc. of 0.1 N $Na_2S_2O_3$ solution are consumed, then $(1.5\,i - t)\frac{58.05}{6 \times 10^4}$ g. of thiocyanate and $(t - 0.5\,i)\frac{126.91}{2 \times 10^4}$ g. of iodide iodine have been found.

Thiocyanate and Cyanide Together [(47) III]. The thiocyanate is determined alone in one sample, and the sum of the two materials is measured in a second sample by the bromometric Method B. However, both materials may be determined directly after each other in the same sample. To accomplish this the solution of the sample measuring about 100 cc. and about 1.2 N with respect to HCl, is treated with about 0.4 g. of solid, pure iodine cyanide previously dissolved in very little alcohol. After waiting a short while until a copious separation of iodine demonstrates that the thiocyanate has been pre-oxidized, starch is added and the system titrated with iodate until the color is discharged. One gram of potassium bromide is added immediately, and the cyanide determined by the bromometric Method B as given on p. 85. If p cc. of 1/40 M iodate is used in the titration of the thiocyanate, and q cc. in the bromination, then $p\frac{58.05}{6 \times 10^4}$ g. of thiocyanate (CNS) and $\left(q + \frac{p}{6}\right)\frac{13}{10^4}$ g. of cyanogen (CN) have been found. The term $\frac{p}{6}$ arises from the fact that in the titration of thiocyanate hydrogen cyanide is consumed; according to equation (*17*) six times as much iodate is consumed by hydrogen cyanide as in reaction (*16*). Therefore the method can be used only when not more than two moles of thiocyanate are present to each mole of cyanide, or if by the addition of a known quantity of cyanide the ratio of cyanide to thiocyanate is brought to at least 1 CN : 2 CNS. The method can be used for any small quantity of cyanide if the titration is made with periodate instead of iodate, for in this case no hydrogen cyanide is consumed in oxidizing the thiocyanate:

$$CNS^- + IO_4^- = ICN + SO_4^{--}.$$

The titration with periodate requires that 1 g. of KBr be added as catalyst at the very start of the titration of the thiocyanate. The bromide bridges over the reaction resistance to the first stage of the periodate reduction: $IO_4^- \rightarrow IO_3^-$. One cc. of 1/60 *M* periodate solution corresponds to $\frac{58.05}{6 \times 10^4}$ g. of CNS and to $\frac{13}{10^4}$ g. of CN.

Ferrocyanide [(47) III] is one of those materials whose oxidation by iodate proceeds more slowly than the succeeding reaction (*5*). The direct titration is successful only after a pre-oxidation with hypoiodous acid. It is more convenient to carry out the determination with the aid of an excess, using Method B. Up to about 30 cc. of 0.1 *N* ferrocyanide solution is treated with 50 cc. of 2.5 *N* HCl, 45 cc. of 1/40 *M* iodate solution is added, the mixture allowed to stand closed for 20 minutes, and then titrated back with arsenious acid. One cc. of 1/40 *M* iodate corresponds to 1 cc. of 0.1 *M* ferrocyanide solution.

Thiocyanate, Cyanide, and Ferrocyanide Together [(47) III]. The solution of the three materials, 1 *N* with respect to HCl, is treated with zinc sulfate which precipitates the ferrocyanide. Without filtering, the thiocyanate and cyanide are titrated successively as already described. The ferrocyanide is determined in a separate sample after it has been oxidized to ferricyanide by permanganate in normal sulfuric acid solution. The unused oxidizing agent is removed with nitrite and urea, and the ferricyanide is then determined iodometrically by titration with thiosulfate.[10]

In this connection, attention is called to the iodometric methods developed by the writer for titrating cyanogen compounds and halides in the presence of each other.[11]

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[10] Lang, Z. anorg. allgem. Chem. *138,* 271 (1924).

[11] Lang, Z. anal. Chem. *65,* 1 (1925).

Hydrogen Peroxide (47 III) may be titrated directly with iodate after oxidation with hypoiodous acid ($ICl + NaOH$). A mixture of 5 cc. of 0.5 *M* iodine monochloride and 20 cc. of 2.5 *N* sodium hydroxide is added without delay to the hydrogen peroxide solution, and swirled for a brief time. The solution is immediately reacidified with 25 cc. of 1:1 hydrochloric acid, 11 cc. of potassium cyanide solution introduced and the titration made with iodate. The oxygen liberated does not interfere. The following equations give the basis for the calculation:

$$2\,HOI + 2\,H_2O_2 = 2\,H_2O + 2\,I^- + 2\,H^+ + 2\,O_2$$

$$2\,I^- + IO_3^- + 3\,HCN + 3\,H^+ = 3\,ICN + 3\,H_2O$$

Therefore, 1 cc. of 1/40 *M* iodate corresponds to 1 cc. of 1/20 *M* hydrogen peroxide solution. Compare also the method of Jamieson (26).

Hydrazine and Its Derivatives (6, 12, 17, 18, 38, 40, 47 III, 73, 118). The writer has found that it is better to titrate hydrazine by Methods A_2 and B, rather than by A_1, because strong hydrochloric acid retards the separation of iodine. It is best to titrate drop by drop. The oxidation products are nitrogen and water. By Methods A_1, A_2 or B, each cc. of 1/40 *M* iodate solution corresponds to 0.000800 g. of N_2H_4. If hydrazine is to be determined along with iodide, the titration by Method B is followed by one with thiosulfate. If i cc. of 1/40 *M* iodate and t cc. of thiosulfate are used, $(1.5\,i - t)$ 0.0008 g. of N_2H_4, and $(t - 0.5\,i)$ 0.006346 g. of iodide iodine have been found. Compare p. 81 for titrations in the presence of mercuric salt.

Hydrazine and Azide. The writer (unpublished studies) has found that hydrazine may be titrated smoothly by Method B, even when considerable quantities of alkali azide are present. In order to determine the latter, the hydrazine and azide are both ozidized to nitrogen and water in a separate sample by ceric sulfate. The difference between the ceric and iodate consumption represents the azide. The determination with ceric sulfate, when an excess is used, is carried out as follows: The reaction flask has a short cylindrical vessel sealed to its inner base. The neutral mixture of hydrazine salt and azide is run into the inner vessel. From a burette, 45 cc. of 0.1 *N* ceric solution is run into the outer vessel, followed by 5 cc. of 0.5 *M* iodine monochloride solution and 5 cc. of concentrated hydrochloric acid. The flask is then closed gas tight, the liquids are mixed, and allowed to stand 10 minutes. Ten cc. of 0.5 *N* potassium cyanide is added, 2 drops of 0.1 *N* ferroïn solution, and the titration made with 0.1 *N* arsenious acid solution, which is added in rather large portions until the yellow liquid becomes permanently brown. The titration is then continued with ceric sulfate solution until the liquid is sharply and permanently decolorized. Both materials may also be determined in sequence in a single sample by iodate and ceric titrations if through proper arrangement, care is taken that the hydrazoic acid is not lost through volatilization.

Hydrazine and Hydroxylamine Together (47 III). Hydrazine may be titrated in sulfuric acid solution by Method B without any hydroxylamine being oxidized if not more than the equivalent of 0.07 g. of $NH_2OH.HCl$ per 150 cc. is present. After removal of the iodine cyanide formed, the hydroxylamine can be titrated with permanganate by the ferric ammonium sulfate method,[12] whereby the hydroxylamine is oxidized to nitrous oxide and water. The salt solutions are run into a 500 cc. boiling flask, acidified with 50 cc. of 5 *N* sulfuric acid, 5 cc. of potassium cyanide is added, starch introduced, the solution diluted to 150 cc. and titrated dropwise with iodate until the deep blue of the iodine-starch lightens. Two grams of sodium chloride is then added and the titration continued to a sharp end point. Thereupon the iodine cyanide is reduced with 0.1 *N* sulfite solution, which is added dropwise to the swirled solution until the iodine-starch color just disappears. The iodide that has formed is then precipitated with silver nitrate solution. Thirty cc. of saturated ferric ammonium sulfate is added, the solution is heated to boiling and boiled for 8 minutes. After cooling, manganous sulfate solution is added and the titration made with permanganate. One cc. of 1/40 *M* KIO_3 corresponds to 0.000800 g. of N_2H_4, while 1 cc. of 0.1 *N* $KMnO_4$ solution indicates 0.00165 g. of NH_2OH.

Selenium [(47) III]. *Selenious acid* may be determined by the following method based on the principle announced by Strecker and Schartow (121). Selenite solutions containing not more than 0.06 g. of selenium are treated with 50 cc. of 1/40 *M* hydrazine sulfate solution, brought to a sulfuric acid concentration of 1–2 *N* and boiled for 5 minutes. After cooling, 2 g. of sodium chloride and 5 cc. of potassium cyanide solution are added and the solution titrated with iodate, in the presence of starch, until the color changes. In solutions not too strong with sulfuric acid, selenious acid is reduced smoothly:

$$SeO_3^{--} + N_2H_4 + 2\ H^+ = Se + 3\ H_2O + N_2.$$

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[12] Raschig, Ann., *241*, 191 (1887).

Lower values are obtained in hydrochloric acid or stronger sulfuric acid solutions. One cc. of 1/40 *M* hydrazine solution corresponds to $\frac{78.96}{4 \times 10^4}$ g. Se.

Potassium selenocyanide containing a maximum of 0.08 g. of selenium is treated with 10 cc. of iodine monochloride, and titrated by Method A_1, after adding concentrated hydrochloric acid (writer's unpublished studies). According to the equation:

$$SeCN^- + IO_3^- + H^+ = SeO_3^{--} + I^+ + HCN$$

1 cc. of 1/40 *M* iodate solution is equivalent to $\frac{104.96}{4 \times 10^4}$ g. SeCN.

Sulfur Compounds. Jamieson (21, 23) titrates *sulfite,* also *thiosulfate* and *tetrathionate* by Methods A, whereby these materials are oxidized to sulfate. Dean (22) titrates *heavy metal sulfides* by the Andrews method. One-third of the sulfide sulfur is oxidized to sulfate and the rest separates as free sulfur. Haller (30) determines *sulfurous acid* in gas mixtures by the Andrews method, after the sulfurous acid has been absorbed previously in sodium hydroxide solution containing glycerine. The determination of sulfurous acid, employing the iodate reduction of equation (*1*), was carried out by Schwicker (4), by Hendrixon (44) and by Bonner and Yost (53). If atmospheric oxygen is excluded, the method is exact. Compare also (50).

Hypophosphorous and Phosphorous Acids. According to Brukl and Behr (39) a solution of these materials, which must contain no nitric or hydrochloric acid, is weakly acidified with sulfuric acid, and then treated with 2.5% iodic acid solution, using 0.25 g. of iodic acid for each 0.1 g. of hypophosphorous acid and half this quantity for phosphorous acid. Then the iodine is removed completely by boiling, the cooled solution treated with 2 g. of potassium iodide and then titrated back with thiosulfate. The calculation is based on the fact that four moles of HIO_3 are consumed in the oxidation of five moles of H_3PO_2, whereas five moles of H_3PO_3 are equivalent to two moles of HIO_3. Compare also (75).

Chlorate, Chromate and Vanadate. Andrews (8, 9) allowed potassium iodide to react for 10 minutes on chlorate, in at least 1:2 hydrochloric acid, in a tightly closed flask. More than three moles of iodide should be taken per mole of chlorate. The excess iodide is then titrated back with iodate according to his method. The results are not affected by 24 hours standing before measuring the excess. One cc. of 0.1 *M* potassium iodide solution corresponds to 1 cc. of 1/30 *M* chlorate solution.

Andrews (8, 9) determined chromate similarly. Somewhat more than three moles of iodide should be used for two moles of chromic acid. The back-titration should be made immediately after mixing the reagents. He made no statement concerning the effect of atmospheric oxygen.[13] Probably it is of no significance since, when the given molar relationship is maintained, the excess of iodide is quite small. One cc. of 0.1 *N* potassium iodide solution corresponds to 1 cc. of 1/15 *M* monochromate solution.

Swift and Hoeppel (67) determine vanadate by reduction to vanadyl salt by means of potassium iodide, whose excess is titrated back by Andrews method. The hydrochloric acid concentration must be 6–8 *N* and air must be excluded.

Arsenious and Antimonous Salt. It is best to titrate by Method A_2 (88) or B [(47) II]. The hydrolysis of the antimony salt is prevented by adding tartaric acid or sodium pyrophosphate. The antimony salt will stay in solution even without these, if the sample contains 15% by volume of concentrated hydrochloric acid. Method A_1 is less suited for the titration because strong hydrochloric acid retards the liberation of the iodine, which Mutschin (90) found was a considerable hindrance when titrating antimony. A lowered consumption of iodate, in this case, may be overcome by adding 5 cc. of iodine monochloride solution and by delaying the final titration somewhat. One cc. of 1/40 *M* iodate solution corresponds to 0.003746 g. of As or 0.006088 g. of Sb. For applications see (8, 9, 16, 28), for the potentiometric titration (79, 90), and concerning the titration in the presence of mercury salt, p. 81.

Arsine and Free Arsenic. According to Kubina (64) arsine, AsH_3, is determined by Method B, after pre-oxidation with iodine monochloride. Ten cc. of iodine monochloride and 50–100 cc. of about 2.5 *N* hydrocloric acid are placed in a flask of about 500 cc. capacity and fitted with a ground-in capillary cock (Fig. 2, p. 100). The flask is then evacuated, a definite volume of the gas containing arsine drawn in and thoroughly shaken for several minutes. After adding some water and 1 g. of potassium cyanide, starch is introduced and the titration is made with iodate solution. The summation of the reactions gives:

$$AsH_3 + 2\,IO_3^- + 2\,HCN = AsO_4^{---} + 2\,ICN + H^+ + 2\,H_2O.$$

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[13] Compare Böttger and Böttger, Z. anal. Chem. *69,* 145 (1926).

1 cc. of 1/60 *M* iodate solution corresponds to 0.1866 cc. of AsH_3 (0° C., 760 mm.). Gangl and Sánchez (82) have shown that free arsenic after being dissolved in iodine monochloride solution can also be titrated with iodate.

Tin. If stannous chloride solution is titrated with iodate by Method B there are two stopping places. The first point, characterized by the solution's becoming blue, is reached when all of the stannous salt has just been oxidized in accordance with the equation:

$$3\ Sn^{++} + IO_3^- + 6\ H^+ = 3\ Sn^{++++} + I^- + 3\ H_2O. \qquad (18)$$

The second point, which may be recognized by the discharge of the color, shows the completed oxidation of the iodide formed in reaction (*18*):

$$2\ I^- + IO_3 + 3\ HCN + 3\ H^+ = 3\ ICN + 3\ H_2O. \qquad (19)$$

The total reaction may be represented:

$$2\ Sn^{++} + IO_3^- + HCN + 5\ H^+ = 2\ Sn^{++++} + ICN + 3\ H_2O. (20)$$

The iodate consumed in the two stages is exactly 2:1. The net reaction (*20*) can be used advantageously in the titration of pure stannous solution. Atmospheric oxygen participates in the partial reaction (*18*) and increasingly so the more slowly the titration is made. This action may be minimized by rapidly running in the iodate solution past the first point. The titration then can be carried slowly to the discharge of the color because atmospheric oxygen no longer interferes.

Jamieson (24) however, used Method A_1 for such gross titrations when determining stannous chloride and also metallic tin. Ramsey and Blann (85) describe a method of determining stannous tin in which the titration is based on equation (*18*).

Tin and Antimony Together. When analyzing mixtures of stannous chloride and antimonous chloride, first the sum of the two is determined by means of the rapid gross titration of the tin, using Method B and excluding the air (writer's unpublished study). In this it is best to add the potassium cyanide only after the partial reaction (*18*) has occurred, that is, after the blue coloration has appeared. The titration to the discharge of this color may then be accomplished in the presence of air. The sum of the iodine cyanide and the quinquivalent antimony salt is titrated then with thiosulfate.[14] To this end, the hydrochloric acid concentration is brought up to 1:5, and the solution titrated with 0.1 *N* thiosulfate, adding the potassium iodide (2 g.) only toward the end. If i cc. of 1/40 M iodate solution and t cc. of 0.1 N thiosulfate are used, $(t - 0.5\,i)\,\frac{121.76}{2 \times 10^4}$ g. of Sb and $(1.5\,i - t)\,\frac{118.7}{2 \times 10^4}$ g. of Sn have been found.

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[14] Kolb and Formhals, Z. anorg. Chem. *58*, 202 (1908).

In analytical practice, the usual demand is for the determination of tin and antimony in mixtures of stannic and antimonous chlorides. In this case, the procedure given on p. 103 may be followed, titrating with iodate instead of bromate, the antimony by Method B, and the tin according to the partial reaction (*18*). The gross titration, equation (*20*), can not be applied in this case, since the free antimony liberated and also any antimonous salt that might be still in solution would be included.

Copper. Jamieson (15, 27) precipitates copper as cuprous thiocyanate, filters and washes the precipitate, and then titrates by Method A_1. The reaction can be expressed:

$$4\ CuCNS + 7\ IO_3^- + 10\ H^+ + 6\ Cl^- = 4\ Cu^{++} + 4\ SO_4^{--} + 3\ ICl_2^- + 5\ H_2O.$$

Accordingly, 1 cc. of 1/40 M iodate solution is equivalent to $\frac{63.57}{7 \times 10^4}$ g. of Cu.

In order to determine copper by Method B[(47) II] the ammoniacal solution is reduced with potassium cyanide, then oxidized in weakly acid solution with iodine monochloride and finally titrated with iodate. The writer (unpublished results) determines copper in white metal as follows: 1 g. of the alloy is dissolved by boiling with a mixture of 20 cc. of hydrochloric acid and 4 cc. of nitric acid. The solution is diluted to 50 cc. and the lower oxides of nitrogen are removed by adding urea. When the cooled solution no longer smells of these oxides, 5–6 g. of crystallized sodium pyrophosphate is added and after this salt has dissolved the solution is made alkaline with ammonia water. The pyrophosphate keeps all the heavy metals in solution. The color is now discharged with 0.5 N potassium cyanide solution, at least 10 cc. being added. The solution is then acidified with 2.5 N hydrochloric acid, adding 5–10 cc. more than is required to produce the permanent precipitation of cuprous cyanide. Five cc. of iodine monochloride is added and the cuprous cyanide soon goes into solution. Finally 20–30 cc. of hydrochloric acid (1:1) is added, then starch solution and the titration is made with iodate. The solutions of alloys containing much lead do not become entirely clear on the addition of iodine monochloride, but this is no disadvantage. The heavy metals: Bi, Sb, Sn, Zn, Cd, Fe, which may also be encountered in these alloys, do not affect the procedure. One cc. of 1/40 *M* iodate solution corresponds to $\frac{63.57}{10^4}$ g. of Cu.

Iron (47, II). The oxidation of ferrous salt with iodate proceeds more slowly than the succeeding reaction (*5*). Therefore, the titration of a ferrous salt requires either pre-oxidation with ICl or HOI, or else the use of an excess, whose determination is best made by the bromometric Method B. The pre-oxidation with iodine monochloride and the direct titration are carried out as follows: Up to about 25 cc. of approximately 0.1 *N* ferrous solution is treated with 10 cc. of iodine monochloride, and allowed to stand closed for 30 minutes. Five to ten cc. of concentrated hydrochloric acid is then added and the solution titrated with iodate in the presence of starch until the dark solution lightens. Thereupon 16 cc. of acidified potassium cyanide solution is added, and after the blue color has developed, the volume is brought to 100–150 cc., and the solution titrated to a sharp end point. Heisig (58) determines ferrous iron by Method A_1, adding iodine monochloride. One cc. of 1/40 *M* iodate solution corresponds to $\frac{55.84}{10^4}$ g. of Fe.

Ferrous and Arsenious Salts Together. Arsenious and ferrous salts can be titrated with iodate, one after the other in sulfuric acid solution [(47) II]. The writer (unpublished results) has found that in hydrochloric acid solution, the ferrous salt can be titrated first if some sodium fluoride is added. This titration is made with 0.1 *N* vanadate, and diphenylamine is used as indicator. After reducing the diphenylamine blue with a trace of ferrous salt, the trivalent arsenic can be titrated by Method B, taking care to acidify the cyanide solution before adding it. Obviously it is still simpler to successively titrate the two materials with ceric sulfate, using Gleu's procedure.[15]

Titanium, Vanadium, Molybdenum, Tungsten, Uranium. Some of the lower oxidation stages of these metals reduce iodate and iodine monochloride only slowly. If cupric or ferric salt is used as intermediary, the reduction proceeds rapidly. For the determination, the approximately 1 *N* hydrochloric acid solution of quadrivalent titanium or quadrivalent vanadium salt or vanadate is run through a reductor charged with electrolytic cadmium. The reduced solution is dripped into 10 cc. of iodine monochloride solution containing 15 cc. of potassium cyanide solution and 5 drops of 0.5 *M* copper sulfate solution. The receiving solution is kept under an atmosphere of carbon dioxide. Then the titration is carried out by Method B. When determining molybdenum the molybdate solution is treated in the same way, but neither potassium cyanide nor copper sulfate is added to the iodine monochloride, but instead 5 cc. of 0.5 *M* ferric chloride solution. The titration is made by Method A_1. The Ti(III), V(II), Mo(III) produced in the reductor are oxidized in the subsequent reaction to Ti(IV), V(IV), Mo(VI). On the other hand, Berry (80) found that V(II) is oxidized to V(III) when the cyanide procedure is used in the absence of other metals, and Jamieson (25) found that if the iodine monochloride method is used with a solution containing no iron, Mo(III) is oxidized to Mo(V). The determination of tungsten requires reduction of the concentrated hydrochloric acid solution of the tungstate to W(III) by means of liquid lead amalgam.[16] The further treatment is like that used with the Ti(III) salt, but it is expedient to use more (5 cc.) copper sulfate solution. W(III) is oxidized to W(VI). Before titrating, the solution is diluted until the content of hydrochloric acid is about ten volume per cent.—Uranium (IV) is oxidized to uranyl salt with iodine monochloride and ferric chloride solutions and titrated by Method A_1.

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[15] Gleu, Z. analyt. chem., *95*, 305 (1933).

Thallium. Berry titrates thallous salts with iodate (52) and also, after a pre-oxidation by iodine monochloride, with ceric sulfate (62), or using Method A_1 with chloramine-T. Method B is not applicable because of the failure of the iodine-starch reaction. Swift and Garner (91) confirmed the accuracy of the iodate titration, but found overconsumptions when the titration was made with ceric sulfate or with permanganate in the presence of iodine monochloride.

Mercury. Jamieson (19) has shown that mercurous chloride can be titrated directly by Method A_1. For the determination of mercuric salt he (31) precipitates the metal quantitatively as $HgZn(CNS)_4$ and titrates the thiocyanate in the precipitate. The procedure is as follows: The mercuric solution is treated with 25 cc. of the precipitating reagent and then diluted to 75 cc. (The precipitant contains 39 g. NH_4CNS + 29 g. of $ZnSO_4$ in 1 liter of water). The walls of the beaker are rubbed with a glass rod until the crystallization starts, and after standing 5 minutes the suspension is vigorously stirred for 1 minute. After an hour the suspension is filtered and the precipitate washed with a mixture of 10 cc. of the reagent diluted with 450 cc. of water. The paper and precipitate are placed in a stopper flask along with 35 cc. of concentrated hydrochloric acid, 10 cc. of water and 7 cc. of chloroform and titrated with an iodate solution (19.2191 g. of KIO_3 per liter). One cc. of potassium iodate of this concentration corresponds to 0.003 g. of Hg.

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[16] Someya, Z. anorg. Chem. *145,* 168 (1925).

The writer (unpublished results) determines mercury in mercuric chloride, cyanide or nitrate as follows: The mercury is liberated from the neutral mercuric solution by treatment with 4 cc. of formaldehyde (35% solution) and 10 cc. of 5 *N* potassium hydroxide solution. The volume of the reaction mixture should not exceed 50 cc. The sample is swirled occasionally over a period of 10 minutes, then acidified with 15–20 cc. of hydrochloric acid (1:1). Then 10 cc. of iodine monochloride solution is added, which oxidizes the mercury almost instantly to the divalent condition. After about 1 minute, 80 cc. of concentrated hydrochloric acid and 5 cc. of chloroform are added, and the cooled solution is titrated then by Method A_1. According to the equation:

$$2\,Hg + IO_3^- + 6\,H^+ = 2\,Hg^{++} + I^+ + 3\,H_2O$$

1 cc. of 1/40 *M* iodate solution corresponds to $\frac{200.6}{2 \times 10^4}$ g. of Hg.

Zinc. Jamieson (29) determined zinc by a method analogous to that used for mercury. The zinc is precipitated as $ZnHg(CNS)_4$, and the thiocyanate in the precipitate is then titrated. The precipitating agent is a solution containing 39 g. of KCNS + 27 g. of $HgCl_2$ per liter of water. See 84 for application.

Cadmium and Bismuth. Berg and Wurm (56) precipitate cadmium as the naphthoquinoline salt of cadmium hydroiodide

$$(C_{13}H_9N_2) \cdot H_2\ [CdI_4],$$

and bismuth as the o-oxyquinoline salt of bismuth hydroiodide, $(C_9H_7ON)\ .\ H[BiI_4]$, and titrate the iodide in these precipitates by Method B or C. The sensitivity for the precipitation of cadmium is about 1:560,000, for bismuth, 1:700,000–1:1,400,000.

They determine *cadmium* as follows: The cadmium sulfate solution is treated with 50 cc. of 2 *N* sulfuric acid, 50 cc. of 10% sodium tartrate solution and sufficient 2.5% solution of β-naphthoquinoline in 0.5 *N* sulfuric acid. A drop of dilute sulfur dioxide solution is added and the cadmium precipitated by the addition of an adequate volume of about 0.2 *N* potassium iodide solution. The total volume should be about 150 cc. After 15–20 minutes the suspension is filtered, the precipitate sucked as dry as possible and washed with a freshly prepared mixture of the following composition: 10 cc. of the 2.5% naphthoquinoline solution in 0.5 *N* sulfuric acid diluted to 90 cc. with water and 10 cc. of 0.2 *N* potassium iodide. The first 2 or 3 washings are made with this wash liquid to which 2–3 cc. of 0.2 *N* potassium iodide solution has been added. The precipitate is sucked dry again and decomposed with 20 cc. of 2 *N* sodium hydroxide or ammonium hydroxide and then made just acid. The acid concentration is brought up to 1.2 *N* and the titration made by Method B or C. One cc. of 1/60 *M* iodate solution corresponds to 0.9367 mg. of Cd. The determination may be made in the presence of 0.3–0.4 g. of the following metals, which must be present as sulfate: Co, Ni, Mn, Zn, Fe (III), Cr (III), Al. See the original paper concerning the separation of cadmium from tin and antimony. Pass and Ward (78) use this method for the determination of cadmium in metallic zinc and in zinc ores.

Berg and Wurm (56) give the following directions for the determination of *bismuth.* The cold bismuth solution which is acidified slightly with sulfuric or nitric is treated with an excess of 5% solution of o-oxyquinoline in 0.2 *N* sulfuric acid. Then an approximately 0.1 *N* potassium iodide solution is dropped in until the precipitate of the o-oxyquinoline salt of bismuth hydroiodide agglomerates. The filtration is made at once, and a wash liquid of the following composition is used: 50 cc. of 2 *N* sulfuric acid, 25 cc. of 0.1 *N* potassium iodide solution, 1.8 g. of o-oxyquinoline and a pinch of hydrazine sulfate are dissolved and made up to 1 liter. The washed precipitate is sucked dry, dissolved in 10% hydrochloric acid and titrated with iodate. One cc. of 1/60 *M* iodate solution corresponds to 1.7417 mg. of Bi. The method is excellent for the volumetric determination of even less than 1 mg. of bismuth. Small quantities are titrated with 1/300 *M* iodate solution. Berg and Wurm have used the method also in the presence of Cd, Fe (II), Ni, Co, Mn, Zn, Cr (III), Al, Mg, As (III), all present as sulfates, and with appropriate modifications also in the presence of Cu (II), Fe (III), Sb, and Sn. Hg, Ag, Pb, Tl, and larger quantities of hydrochloric acid interfere.

Organic Compounds. Of the organic acids, *oxalic acid* is exceptional because it is oxidized smoothly by excess iodate in hot, *dilute sulfuric acid* to carbon dioxide and water (Millon's Reaction). The iodate is reduced in accordance with equation (*2*). Rosenthaler (35) employed this reaction to standardize iodate solution with oxalic acid. The reaction is autocatalytic and is retarded by hydrogen cyanide, in whose presence the catalytically active reduction stages, I and HOI, go over into the catalytically inactive ICN.[17]

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[17] Warburg, Biochem. Z. *174,* 497 (1926); Wieland and Fischer, Ber. *59,* 1171 (1926); Fischer and Wagner, Ber. *59,* 2384 (1926).

In *concentrated sulfuric* acid solution all organic compounds are oxidized by iodic acid. This oxidizing action was used by Strebinger (32, 36, 42, 55) and Vortmann (49) for ultimate organic analyses, but it offers no possibilities for specific determinations.[18]

Formaldehyde (88). Twenty cc. of 0.05 *M* formaldehyde solution is treated in a 300 cc. measuring flask with 5 cc. of 0.5 *M* iodine monochloride solution and 20 cc. of cold 2.5 *N* sodium hydroxide in which is dissolved 15 g. of potassium bromide. After 10 minutes, which suffices for the complete oxidation of the aldehyde to formate, a saturated solution of 22 g. of potassium bromide is added, the solution is acidified with 10 cc. of concentrated hydrochloric acid, diluted to 200 cc., and titrated by Method A_2. One cc. of 1/40 *M* iodate solution indicates 0.001501 g. of H_2CO.

Polyatomic alcohols, according to Malaprade (59, 60) can be quantitatively oxidized at room temperature to formaldehye and formic acid by periodic acid. The periodate is reduced only to iodate. Each mole of these alcohols with n carbon atoms requires for oxidation $(n-1)$ moles periodate, and produces 2 moles of formaldehyde and $(n-2)$ moles of formic acid. The lowest member, glycol $(n=2)$, produces, accordingly, 2 moles of formaldehyde and no formic acid. The measured quantity of the alcohol, is treated with 50 cc. of periodate solution (standardized against thiosulfate) and several cc. of 4 *N* sulfuric acid. After 2–3 hours, potassium iodide is added and the back-titration made with thiosulfate. The difference between the thiosulfate consumption before and after the oxidation measures the periodate consumed. This can be recalculated by the given relationship to moles of the polyatomic alcohol. In this way, Malaprade determined glycol, glycerine, erythrite, adonite, and mannite. Compare also (76, 86).

BROMATE METHODS

In general, titrations with bromate can be carried out more simply than those with iodate. Consequently, and also because of the comparatively low price of bromate, these methods are preferred in analytical practice to those employing iodate. Certain titrations, which are based on the greater oxidizing power of bromate, are not even possible with iodate. On the other hand, the bromate methods lack that differential control of the course of the reaction which put the iodate methods in a special class.

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[18] Compare Cuny and Robert, concerning the oxidation of xanthyl compounds with iodic-sulfuric acid, J. pharm. chim., *11*, 241, 337 (1930).

The reduction of bromate ordinarily goes smoothly clear to bromide, since all the intermediate stages are strong oxidizing agents. At the end of the titration free bromine appears,

$$5\ Br^- + BrO_3^- + 6\ H^+ = 3\ Br_2 + 3\ H_2O$$

which indicates the end point by destroying the dye stuff indicator. *Methyl orange, methyl red and indigo carmine* have proved to be excellent *indicators* in these methods. Many other dyes have been proposed, but there would be little point in naming them here. Mere reference will be made to the paper of Smith and Bliss (139) who with this use in mind tested several monoazo- and triphenylmethane dyes that are particularly not fast to halogens. The quantity of bromate consumed by the indicator is extremely small, and when titrating with 0.1 *N* solution need not be taken into account. The indicator change is an irreversible reaction, which obviously must proceed more slowly than the oxidation of the material being determined.

Reversible indications, that may be used in suitable cases, are the color of bromine which appears at the end point, the iodine-starch reaction, and the heterogeneous indication proposed by Winkler.[19] This consists of carbon tetrachloride colored violet by 2 drops of a saturated aqueous solution of iodine. At the end point, the iodine is oxidized, and the carbon tetrachloride becomes colorless. Schulek (163) uses α-naphthoflavone as reversible indicator; at the equivalence point it takes on a decided rust-brown color. The mechanism of this indication has not been elucidated completely as yet, but in any case colloidal phenomena play a part, because the color change is more pronounced when more of the indicator remains in colloidal solution. Schulek titrates arsenious and antimonous salts in sulfuric acid solution containing bromide, adding 2 drops of 0.5% solution of α-naphthoflavone in 96% alcohol. If the hydrochloric acid content exceeds 5%, the sensitivity of the indicator is decreased. Uzel (164) titrates stannous tin and hydrazine salt in the same way, but uses, at the same time, starch solution to raise the sensitivity. It has been the writer's experience that titrations may be made when the content of hydrochloric acid is as much as 20% by volume, if 10–20 drops of 0.5% α-naphthoflavone solution is used as indicator; the solution being titrated should contain at least 0.5 g. of potassium bromide per 100 cc. Szebellédy and Schick (159) use colloidal red selenium as a reversible redox indicator in the titration of arsenite.

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[19] Winkler, Z. anorg. Chem. *28,* 477 (1915); Arch. Pharm. *265,* 554 (1927).

Direct titrations with bromate in the presence of irreversible dye stuff indicators are made without exception in hydrochloric acid, whereby the chlorine liberated according to the equation:

$$10\ Cl^- + 2\ BrO_3^- + 12\ H^+ = 5\ Cl_2 + Br_2 + 6\ H_2O$$

enters into action. The hydrochloric acid concentration should in general be at least 1.5–2 *N*. The titration ought to be carried out drop by drop so that the indicator change, which is a time reaction, may be sharply detected. If determinations are to be executed rapidly, the volume of bromate to be used must be known approximately, since ordinarily with irreversible dye stuff indicators there is no way of ascertaining when the end point is close at hand. Rapid titrations may be accomplished also through back-titration of excess. The bromate solution is added quickly to the sample in hydrochloric acid until the solution becomes distinctly yellow. The color is then discharged with arsenious acid and after adding the indicator the final titration is made with bromate to a sharp end point.

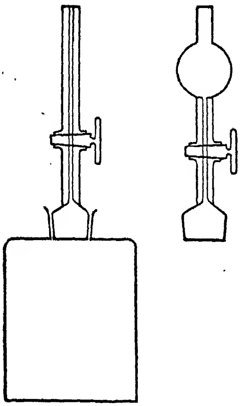
FIG. 2

The flasks devised by Treadwell and Mayr (101), shown diagrammatically in Figure 2, have proven their worth in determinations involving *excess bromate,* when the reaction time is rather long. These flasks, ½–1 liter in capacity, are fitted with a ground-in capillary carrying a stop cock, or with a bulb tube through which they can be evacuated. Chlorine or bromine can not escape from these vessels. The neutral solution of the sample is placed in the reaction flask along with excess bromate or, in case of bromination, with a solution of bromate and bromide. The flask is evacuated, closed, an adequate quantity of hydrochloric acid introduced through the capillary stopper, rinsed in with water, allowing no air to enter, and then permitted to stand closed. After the proper reaction period, potassium iodide solution is run in, the stopper is removed and the contents of the flask are titrated with thiosulfate, using starch as indicator.

The action of bromic acid in hot halide-free solution is worth considering for certain oxidations. Smith (108) studied the stability of bromic acid in boiling solutions, and found that it is stable in hot solutions containing perchloric, nitric and acetic acids, but less stable in hot solutions of sulfuric or phosphoric acid.

As to the *accuracy of the bromate methods,* the same considerations hold as in the case of iodate. An indicator correction is necessary when titrating with 0.01 N solutions in the presence of dye stuff indicators. This correction can be determined easily by a blank run under the conditions obtaining in the determination concerned. Zintl and Betz (134) recommend the use of potentiometric indication for *micro-titrations with bromate.*

Berry (80) advises chloramine-T in place of bromate for the titration of thallous and antimonous salts. When this is used, potassium bromide is added to the sample.

PARTICULAR DETERMINATIONS

A solution of potassium bromate containing 2.7835 g. per liter is prepared from recrystallized $KBrO_3$ that has been dried at 150° C. The solution ($0.1\ N = 1/60\ M$), like iodate solution, remains stable for an indefinite time. The indicators, methyl orange and indigo carmine, are used in 0.1–0.2% aqueous solution, methyl red in alcohol solution of the same concentration. This latter indicator may be prepared in aqueous solution if its sodium salt, rather than the free acid, is available.

Arsenic and Antimony. Györy (94) devised the titration of As (III) and Sb (III) with bromate in hydrochloric acid solution with methyl orange as indicator. He should be credited with being the first to find, in this titration, the principle of a direct and generally applicable bromate method. Since then the procedure has found increasing use in analytical practice and is now familiar to all who deal with such determinations. According to Jannasch and Seidel (100) the hydrochloric acid concentration should be kept between 5–10%. In this range, according to Zintl and Wattenberg (115), the dye stuff and the potentiometric end points coincide. Even in 20% hydrochloric acid the color indication is not sharp and appears too late, while the potentiometric end point is still correct.

The arsenious or antimonous solution is treated with 20–25 cc. of concentrated hydrochloric acid, diluted to 100 cc., 1–3 drops of methyl orange added, and the titration carried out drop-wise until the color is discharged. One cc. of 0.1 N $KBrO_3$ corresponds to $\frac{74.91}{2 \times 10^4}$ g. of As, or $\frac{121.76}{2 \times 10^4}$ g. of Sb.

The method has been modified by Nissenson and Siedler (95) who titrate the hot solution in the presence of indigo, and by Winkler (103) who titrates in a sulfuric acid solution containing bromide, the color of bromine itself indicating the end of the titration. When indigo is used as indicator the color change is from blue through yellow green to yellow with a reddish tinge.

Zintl and Betz (134) discuss the *potentiometric micro-titration of arsenic.* The limits of the potentiometric determination of arsenic are about those of the Marsh-Liebig test.

If arsenic and antimony are not already in the titratable trivalent condition they can be brought to this state of reduction by the following methods:

1. By dissolving alloys, sulfide precipitates, and ores in concentrated sulfuric acid: the trisulfates of arsenic and antimony result. Precipitated antimony sulfide may also be dissolved in hot, concentrated hydrochloric acid and so converted quantitatively into antimony trichloride.
2. By separation by means of distillation: the trichlorides of these metals pass over.
3. By reduction of solutions of the quinquivalent metals.

Biltz and Biltz [20] discuss in detail the decomposition with concentrated sulfuric acid and also the distillation method. Kurtenacker and Fürstenau [21] made an intensive study of the reduction of arsenic and antimonic acids by sulfurous acid. Järvinen (111) reduces in concentrated sulfuric acid solution with thiosulfate, Schulek and v. Villecz (135) in the same solvent with hydrazine sulfate. These last two use this reduction when determining arsenic in organic materials.

Zintl and Wattenberg (115) have described a potentiometric method for the determination of arsenic and antimony in the presence of each other. It is based on the following principle: The total of the trivalent metals is determined first by titration with bromate. Directly following this the quinquivalent antimony is reduced at the boiling point, under potentiometric control, with titanous chloride. A little copper sulfate is added and the excess of the reducing agent is removed by shaking with access to the air. The antimonous salt alone is titrated then with bromate.

The titration of trivalent arsenic and antimony serves as the basis for a number of procedures employing an excess of these materials. The portions of these salts not consumed in the reduction are titrated with bromate. Thus v. Bacho (103) determined manganese dioxide, lead dioxide, barium peroxide, chlorate, hypochlorite, chromate and permanganate by reducing with arsenious acid and titrating the excess with bromate. Feigl and Schummer (116) determined hypochlorite and ferricyanide by reduction with antimony trichloride and subsequent back-titration. Similar methods have been described by Rupp and Siebler (119, 124) and later by Peters and Deutschländer (127).

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[20] Biltz and Biltz, "Ausführung quantitativer Analysen" Leipzig, 1930, pp. 318, 328.

[21] Kurtenacker and Fürstenau, Z. anorg. allgem. Chem. *212*, 289 (1933).

Arsine. Kubina (64) places an excess of bromate-bromide mixture in the reaction flask (Fig. 2), draws a known volume of the gas into the evacuated flask, follows it with 25 cc. of sulfuric acid (1:5) and shakes thoroughly for at least 5 minutes. Deci-normal arsenious acid is run in until the color is discharged. The final titration is made with bromate. One cc. of 0.1 *N* $KBrO_3$ solution corresponds to 0.28 cc. of AsH_3 (0° C., 760 mm.).

Tin. The most practical bromate titration of divalent tin is that of Oesterheld and Honegger (102), who add potassium iodide and starch. A blue color appears at the end point. Stannic solutions are reduced as described in the following procedures.

Antimony and Tin Together. The analysis of white metal, a matter of technical importance, presents the problem of determining these elements in the presence of each other. It is solved most simply by the method of Oesterheld and Honnegger (102). One gram of the alloy is dissolved in 20 cc. of boiling concentrated sulfuric acid in a 300 cc. beaker covered with a watch glass. The antimony is oxidized to the trivalent condition and the tin to the quadrivalent state. After driving off the sulfur dioxide, cooling, diluting to about 100 cc. and adding 5 cc. of concentrated hydrochloric acid and some methyl orange, the antimony is titrated with 0.1 *N* bromate solution. After standing for 1 hour, the lead sulfate is collected on a Gooch or similar filter, washed with dilute sulfuric acid, then with water, dried and weighed.

If the tin content is not above 30%, the filtrate from the lead sulfate can be used without further treatment. When more tin is present the filtrate is made up to 500 cc., and an aliquot (100 cc.) taken for the tin determination. The reduction of the stannic salts is made best by the Biltz method (122). The stannic solution, in a narrow neck flask of about 1 liter capacity, is treated with 20 cc. of concentrated hydrochloric acid. Eight grams of fragments of zinc foil (about 0.2 x 2 cm. x 1¼ mm. thick) is added and the solution kept at room temperature by immersion in water. The contents of the flask are swirled frequently, and after 20–25 minutes the zinc has dissolved and the tin, which has been set free, floats on the solution as a spongy mass. Now the neck of the flask is washed down with a little water applied in a fine stream from a wash bottle, 4 g. more of zinc fragments is introduced, the flask is closed with a stopper fitted with a Contat-Göckel valve, which is charged with cold, saturated sodium bicarbonate solution to which a knife-point full of the powdered salt is added. The second lot of zinc dissolves slowly and incompletely. After 20 minutes, 70–80 cc. of concentrated hydrochloric acid is added and the remaining zinc dissolves rapidly. The flask is placed on an asbestos centered gauze, in a place protected from draughts, and warmed gently over a low flame. The spongy tin dissolves in about 30 minutes. Antimony and copper remain undissolved. The completion of this solution is indicated when no threads of hydrogen bubbles can be seen rising from the remains of the spongy metal. Then the flask is cooled under the tap, at first without, and then with, swirling. A solution of sodium bicarbonate is kept at hand to recharge the valve if necessary. After the cooling is finished, the stopper and the neck of the flask are rinsed with a solution prepared from 100 cc. of water, 0.2 g. of potassium iodide, 5 cc. of starch solution and 10 cc. of dilute hydrochloric acid, and freed from atmospheric oxygen by sprinkling in a pinch of sodium bicarbonate. The titration with 0.1 *N* bromate solution, to a blue end point, must be made rapidly. One cc. of 0.1 *N* $KBrO_3$ solution corresponds to $\frac{121.76}{2 \times 10^4}$ g. of Sb and $\frac{118.70}{2 \times 10^4}$ g. of Sn. If this theoretical equivalent weight of tin is used an error is introduced, unless all atmospheric oxygen has been excluded; even the bromate solution must be free of oxygen. It is simpler to use the empirical tin value of the bromate solution that is obtained if 0.25 g. of pure tin is dissolved in concentrated sulfuric acid and carried through the same reduction and titration procedure.

Biltz (122) states that the quantitative reduction of stannic salts is only certain if the reduction is carried out, as described, in moderately strong hydrochloric acid. When the reduction is made in acid that is quite strong from the beginning, most of the zinc is used for discharging the hydrogen ion, and the reduction of the quadrivalent tin is incomplete.

Arsenic, Antimony, and Tin in the Presence of Each Other. The separation is accomplished by distillation in which, by maintaining appropriate conditions, trivalent arsenic, trivalent antimony, and quadrivalent tin are obtained successively in the distillate. Obviously, reduction of the stannic salt by the procedure already described must precede the titration. The distillation procedure for arsenic, which originated in the middle of the last century and was fundamentally improved by Fischer in 1881,[22] has been the subject of many investigations. Plato[23] was the first to apply distillation to the separation of antimony and tin. The latest version of the distillation method is the so-called "Breslau Procedure," by Biltz (136). See the original paper for details.[24]

Copper and Bismuth. Zintl and Wattenberg (107) determine copper with bromate potentiometrically. The cupric solution, about 2.5 *N* and free of nitrate, is reduced with a slight excess of titanous chloride and then titrated potentiometrically at 80° C. with bromate. Air must be excluded during all these operations. There are two breaks in the potential curve. The first indicates the completion of the oxidation of the titanous salt, the second that of the univalent copper. The volume of bromate bounded by these two breaks corresponds to the copper present.

Reissaus (131) determines bismuth by an indirect method involving the titration of cuprous salt. In hot solution, containing sufficient hydrochloric acid, bismuth chloride reacts with copper:

$$Bi^{+++} + 3\ Cu = Bi + 3\ Cu^{+}.$$

The cuprous salt is titrated with bromate. The procedure is as follows: First the bismuth is precipitated as oxychloride, this is filtered, washed, transferred to a 500 cc. Erlenmeyer flask, dissolved in 30 cc. of concentrated hydrochloric acid, diluted with water to 200 cc., heated to boiling under an atmosphere of carbon dioxide, and after the air has been expelled completely, copper turnings are added. After boiling for about 15 minutes, a bright copper turning is added to determine whether all of the bismuth has been precipitated—the turning, after a short period of boiling, must remain bright. The filtration is made under carbon dioxide, into a 1 liter flask containing some bicarbonate solution, and the precipitate is washed with hot water containing hydrochloric acid. Methyl orange is added, and the solution titrated hot with 0.1 *N* bromate solution until the color changes from delicate pink to light blue. Lead does not interfere. One cc. of 0.1 *N* bromate corresponds to $\frac{209}{3 \times 10^4}$ g. of Bi.

Iron. Smith and Bliss (140) proceed as follows. The warm solution of the ferric salt, free of nitrate and containing 10 cc. of concentrated hydrochloric acid per 25–50 cc., is reduced by adding stannous chloride solution drop-wise, then diluted with 80 cc. of cold water and cooled to room temperature. The excess stannous chloride is removed with 10 cc. of 10% mercuric chloride solution. Then 10 cc. of a solution containing 4 g. of $CuSO_4 \cdot 5\ H_2O$, 100 g. of $(NH_4)_3\ AsO_4$ and 500 cc. of 85% H_3PO_4 per liter is added. The indicator (fuchsine, chrysoidine R, bordeaux or naphthol blue-black) is introduced and the solution titrated with 0.1 *N* basic mercuric bromate to the disappearance of the color. The copper sulfate acts as catalyst, while the ammonium arsenate retards the oxidation by the air of the cuprous salt produced as an intermediate. According to the authors the method gives exact values, even in the presence of not too large quantities of organic materials; they studied the effect of tartaric, citric, succinic, oxalic and acetic acids. Methyl or ethyl alcohol can be distilled away to a point where they no longer interfere.

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[22] Fischer, Ann. *208,* 182 (1881).

[23] Plato, Z. anorg. allgem. Chem. *68,* 26 (1910).

[24] See also Scherrer, J. Research Nat. Bur. Standards, *16,* 253 (1936).

The authors state that in their procedure the basic mercuric bromate may not be replaced by potassium bromate. The reagent, $HgOHBrO_3$, is prepared, according to Smith (120) by dissolving mercuric perchlorate, $Hg(ClO_4)_2$, in a little water, and adding, slowly and with constant stirring, a half-saturated sodium bromate solution. The basic mercuric bromate crystallizes with no water of hydration, and may be dried at 130–140° C. without decomposition. Its neutral solution or that in dilute nitric or perchloric acid is stable.

Kolthoff (104) gives the following directions for the determination of ferrous salt. Twenty-five cc. of 0.1 *N* potassium bromate solution and 10 cc. of 25% phosphoric acid are added to 10 cc. of the slightly acid 0.1 *N* ferrous solution. The mixture is allowed to stand 5 minutes in a closed vessel, and is treated then with 5 cc. of normal potassium iodide and 2 drops of 3% ammonium molybdate solution. After a further delay of 3 minutes the titration is made with thiosulfate. According to Ostwald[25] the molybdate catalyzes the reduction of bromate by iodide.

Thallium. The oxidation of thallous salt with bromate takes place immediately in hydrochloric acid solution. Zintl and Rienäcker (128) titrate thallous salts with bromate, using methyl orange as indicator. Trivalent thallium must be reduced with excess titanous chloride, and the titration with bromate can be made then potentiometrically. The two breaks define the volume of bromate corresponding to the thallium. One cc. of 0.1 *N* $KBrO_3$ solution indicates $\frac{204.4}{2 \times 10^4}$ g. of Tl.

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[25] Ostwald, Z. phys. Chem. *2*, 127 (1888).

Hydrazine. Kurtenacker and Wagner (105) treat the hydrazine solution with 2–3 g. of potassium bromide and 40 cc. of hydrochloric acid (1:1). The solution is warmed then to about 60° C. and titrated with 0.1 *N* bromate in the presence of indigo, which it is best to add near the end of the titration. Kurtenacker and Kubina (118) determine semicarbazide and phenylhydrazine by this same procedure. Hydrazine is oxidized to nitrogen and water; consequently, 1 cc. of 0.1 *N* $KBrO_3$ corresponds to 1 cc. of 1/40 *M* hydrazine solution.

Hydroxylamine. According to Kurtenacker and Wagner (105) the hydroxylamine solution is treated in the reaction vessel (Fig. 2, p. 100) with an excess of 0.1 *N* bromate solution and acidified with 30 cc. of 1:1 hydrochloric acid. The bromate excess should be at least 10 cc. After 15 minutes, potassium iodide is added and the solution titrated with thiosulfate. Hydroxylamine is oxidized to nitric acid and water; consequently 1 cc. of 0.1 *N* bromate solution corresponds to $\frac{33.0}{6 \times 10^4}$ g. of NH_2OH. Rupp and Mäder (99) oxidize hydroxylamine in moderately strong sulfuric acid solution, with a large excess of bromate-bromide. The reaction time is about 15–30 minutes. Quantities of hydroxylamine exceeding 0.01 g. are incompletely oxidized by bromate-bromide, whereas in strong hydrochloric acid as much as 0.02 g. can be determined smoothly by bromate alone.

Hydrazine and Hydroxylamine Together. According to Kurtenacker and Wagner (105) the total of hydrazine and hydroxylamine is determined in one sample by the method given for hydroxylamine, which involves the use of an excess of bromate. The volume of nitrogen evolved by the oxidation of a second sample with bromate is measured, and the hydrazine content calculated from the volume of gas.

Nitrite. Feit and Kubierschky (93) add the nitrite to excess bromate in sulfuric acid solution, boil off the bromine liberated, cool and titrate back iodometrically. As the nitrite contains small quantities of chloride, the results are too high by a constant amount. Other materials can be determined in this same way, for instance *phosphorous* and *hypophosphorous acids.* Schwicker (4) oxidizes nitrite with excess bromic acid at room temperature and titrates both the bromate excess and the free bromine iodometrically.

Selenium Dioxide. Strecker and Schartow (121) dissolve the weighed selenium dioxide in the minimum volume of hot water, add from a burette a measured volume of 1.2–1.7% hydrazine sulfate solution, and heat rapidly to boiling. The selenium that separates is removed by filtration and the unused hydrazine in the filtrate is titrated by the method of Kurtenacker and Wagner (105). One cc. of 0.1 *N* bromate solution corresponds to $\frac{78.96}{4 \times 10^4}$ g. of Se.

Sulfur Compounds. Treadwell and Mayr (101) oxidize *alkali sulfides* in the reaction flask (Fig. 2, p. 100) with excess bromate-bromide in the presence of at least 25% by volume of hydrochloric acid. The oxidation to sulfate requires about 15 minutes. One cc. of 0.1 *N* bromate solution corresponds to $\frac{34.08}{8 \times 10^4}$ g. of H_2S. The same procedure may be used with *alkali thiocyanates.* Compare also (150).

Hellström (147) determines *organic sulfide acids* with the aid of bromate.

Mayr and Peyfuss (112) determine *sulfurous acid* and *thiosulfate* by the method just given for sulfide, and Kurtenacker and Bittner (123) use this procedure for *tri-, tetra-, and pentathionic acids.* According to them the oxygen of the air interferes in the oxidation of sulfurous acid. Hendrixson (44) found that excluding oxygen in the titration of sulfurous acid with bromate is not sufficient, but that in addition, it is necessary to add a quantity of iodine equivalent to at least 1/6 of the sulfite, in order to prevent the formation of dithionic acid.

Dithionic acid, according to Mayr and Peyfuss (113), can be determined by treating it, in a special apparatus, at the boiling point, with concentrated hydrochloric acid in the presence of a known excess of bromate. During this oxidation a current of air-free carbon dioxide is passed through the solution to carry the excess of free halogen into a receiver charge with potassium iodide solution. The iodine is measured with thiosulfate.

The bromometric determination of mixtures of sulfur acids can not be accomplished without the simultaneous employment of other methods and furthermore it has little significance in view of the availability of the simple and accurate iodine methods of Kurtenacker and Goldbach,[26] which permit the rapid and accurate analysis of even mixtures of *bisulfite, thiosulfate, sulfide, tri-, tetra-,* and *pentathionate.* Only in case *dithionic acid* is to be determined together with other acids of sulfur is it expedient to use bromometric procedures also.

[26] Kurtenacker and Goldbach, Z. anorg. allgem. Chem. *166,* 183 (1927).

Caro's Acid, Persulfuric Acid, and Hydrogen Peroxide Together. Gleu (138) first measures the oxidizing power of the Caro's acid against arsenious acid or hydrobromic acid at room temperature, then titrates the hydrogen peroxide with permanganate, and finally determines the oxidation value of the persulfuric acid at the boiling temperature against arsenious acid. He points out, in detail, that accurate results may be obtained even though the relative quantities are quite varied. The procedure is:

1. *H_2SO_5 Determination.* The weak sulfuric acid solution of the three materials containing about 10–20 cc. of 2 *N* sulfuric acid per 50 cc., is treated with a known excess of 0.1 *N* arsenious acid and then with 5 cc. of 1 *N* potassium bromide solution. After 1–2 minutes, 0.1 *N* bromate is dropped in from a burette until the color becomes yellow because of free bromine. As the bromine continues to appear it is removed immediately, by arsenious acid. At the end, and after a delay of 1 minute, the last trace of the bromine is titrated finally with arsenious acid until the yellow color disappears.

2. *H_2O_2 Determination.* The titrated solution is treated with 5 cc. of 2 *N* manganous sulfate solution and the hydrogen peroxide then titrated with 0.1 *N* permanganate. The end point is indicated by the yellow color due to the free bromine liberated after the oxidation of the peroxide is completed.

3. *$H_2S_2O_8$ Determination.* After the titration with permanganate, a measured excess of arsenious acid is added to the solution. Ten cc. of 20 *N* sulfuric acid is introduced, the solution boiled for 10 minutes and the residual arsenious acid is titrated with bromate.

Iodide, Bromide, and Chloride. The cyanide procedure (directions p. 78) for the determination of iodide may, according to Berg (125), be modified by substituting for the iodate, bromate which is reduced to bromide. The entire titration must be made drop by drop. If a greater volume of bromate is added all at once, any local excess of the oxidant will lead easily to the formation of bromcyanogen also and consequently to high results.

The bromide present may be determined as a sequel to the iodide determination. Berg brings the hydrochloric acid concentration up to 10–15%, drips in 0.1 *N* bromate solution until the transient yellow color, due to free bromine, is discharged. Immediately a mixture of 20 cc. of 10% aniline hydrochloride solution and 10 cc. of about 0.1 *N* potassium bromide solution is added, all at once, to remove the excess of bromate.

After $\frac{1}{2}$–1 minute, the thiosulfate titration, drop by drop, is carried to the discharge of the blue color.

Any bromide originally present and also that formed in the titration of the iodide will be converted into bromcyanogen by the bromate. The titration with thiosulfate, then, represents the sum of this BrCN and of the ICN formed in the determination of the iodide. If b cc. of 0.1 N bromate and t cc. of 0.1 N thiosulfate were consumed in the titrations, then $(t - 1.5\,b)\,\frac{79.91}{3 \times 10^4}$ g. of Br have been found.

It has been the writer's experience that the difficulty in this procedure lies in the correct determination of the excess of bromate. The transient yellow color can no longer be detected when considerable quantities of the bromide remain to be oxidized. It is necessary then to add an excess of bromate, which may easily result in a decomposition of the bromate:

$$BrO_3^- + 2\,Cl^- + 3\,HCN + 3\,H^+ = BrCN + 2\,ClCN + 3\,H_2O.$$

High values result.

Berg (125) uses the reaction represented by the equation just given for an iodometric determination of chloride. In this the bromcyanogen formed, which can be titrated in the presence of the chlorcyanogen, is determined iodometrically and thus gives a measure of the chloride present. In this case, as in the determination of bromide, the bromate serves only as oxidizing agent, not as the standard solution. However, it has been the writer's experience that the iodometric determination of bromcyanogen is not reliable in the presence of large quantities of chlorcyanogen.

Matthes and Brause (130) used Berg's method for determining the iodine and iodide content of tincture of iodine, and Kogan (133) applied it to the determination of bromide in sea water.

Compare p. 75 concerning the titration of iodide with bromate by the iodine-bromide method.

ORGANIC COMPOUNDS

The action of bromate or of bromate-bromide mixtures in acid solution on organic compounds gives rise to three types of effects: (1) oxidation, (2) addition, (3) substitution.

Oxidizing Actions. This is the basis of the determination of the simpler carboxylic *acids* such as *formic,* according to Rupp (13) and of *oxalic* by the method of Feit and Kubierschky (93). These materials are warmed, in dilute sulfuric acid solution, with excess bromate until there is no odor of bromine. The excess bromate is measured iodometrically.

Addition Reactions. These occur when bromine acts on unsaturated compounds. It should be noted that oxidizing actions may occur also if oxidizable groups, aldehyde for instance, are present. The earliest methods for the determination of the halogen binding capacity of unsaturated materials are based on the addition of bromine. Winkler [27] recently worked out methods for the determination of the iodine-bromine number, using bromate-bromide. Vaubel [28] also uses bromate-bromide solution for the determination of iodine numbers. Details are given in the references. Compare also (162).

Substitution Reactions. These may be represented by the scheme:

$$RH + Br_2 = RBr + Br^- + H^+,$$

and consequently involve a divergence in the action of the free bromine. The bromination of aliphatic compounds is applied less often. Consideration must be given to the manner in which the excess bromine is titrated back. If this is done iodometrically, the organically bound bromine may be reduced again, in part or wholly, whereas the organic bromine does not react if the back-titration of the bromine is made with arsenious acid. The simplest example of an aliphatic bromine compound is bromcyanogen; it is reduced by potassium iodide, but not by arsenious acid.

Phenols and Aromatic Amines. These are ordinarily determined by bromination. Koppeschaar (92) has developed this procedure until it can be applied to practically all cases. The back-titration of the excess bromine is made iodometrically, whereby potassium iodide does not reduce bromine which has entered the ring, but does reduce that which has entered the OH group of the phenol.

Vaubel [29] has set up several rules for the bromination of aromatic compounds. No claim is made that they are always valid. Primary phenols and amines always add bromine in the position ortho and para to the OH or NH_2 groups. None of the usual substituents such as CH_3, NO_2, halogen, SO_3H, COOH, N = NR, N = NCl hinder the entrance of the bromine in case they are likewise ortho or para to OH or NH_2. Exceptions are the OH or NH_2 groups themselves, for when they are ortho and para to each other they hinder the direct taking up of bromine. SO_3H and COOH, when ortho or para to OH or NH_2, retard the bromination; a dibrom substitution product is formed first and the tribrom derivative is produced only by the action of an excess. The taking up of the bromine is influenced also by the concentration of the acid, the temperature, the quantity of bromine in excess and the length of time it is allowed to react. Variation in these conditions may, particularly with polynuclear phenols and amines, lead to quite different, highly brominated products. Side reactions, such as oxidation and destruction of the molecule, are influenced also by the experimental conditions. Appropriate control of the temperature, according to Francis and Hill (117), hinders such side actions and also undesired substitution. These writers state that the precipitation of incompletely brominated products, a condition arising particularly with para compounds, can be prevented by the addition of alcohol.

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[27] Winkler, "Ausgewählte Untersuchungsverfahren für das chemische Laboratorium," p. 71, 1931; New series, p. 103, 1936.

[28] Vaubel, Z. angew, Chem. *23*, 2077 (1910); *35*, 679 (1922); *40*, 1143 (1927); Z. Untersuch. Nahr.-und Genussmittel *53*, 151 (1927); *54*, 275 (1927).

[29] Compare Vaubel, "Die physikalischen und chemischen Methoden der quantitativen Bestimmung organischer Verbindungen," Berlin 1902.

Recently Day and Taggart (132) studied the Koppeschaar procedure with respect to its suitability for the determination of a series of phenols, amines and their derivatives. They proceed as follows: A sufficient quantity of the material is dissolved in water, sodium hydroxide or hydrochloric acid, and diluted to 250 cc. Twenty-five cc. of this solution is pipetted into a 500 cc. stopper flask (or bottle) containing 25 cc. of the brominating mixture (75 g. of KBr and 5.6 g. of $KBrO_3$ per liter). The contents of the flask, usually diluted with 50 cc. of water, are treated with 5 cc. of concentrated hydrochloric acid. The flask is closed, shaken for 1 minute, and after standing for the prescribed time, the titration of the excess is made iodometrically. The flask shown on p. 100, which can be evacuated, is better suited for this determination than an ordinary bottle.

The following Table gives the quantity of sample to be taken, the solvent, the dilution of the pipetted aliquot, the bromination period and the number of bromine equivalents reacting per mole of substance. The experiment, in the case of materials which produce tri-bromaniline, should be carried out at a temperature not above 15° C., to prevent oxidation. The same temperature limit applies to sulfanilic and anthranilic acids. Methyl salicylate and phenyl salicylate should be saponified first with sodium hydroxide, and acetyl salicylic acid with water, whereas, acetanilide should be hydrolyzed with hydrochloric acid. Before brominating β-naphthol and thymol, 5 cc. of chloroform should be added as solvent, and an appropriate blank should be run.

Quantity dg.	Substance	Solvent	Dilution cc. H_2O	Bromination Period min.	Bromine Consumed
5–6	Phenol	NaOH	50	5–30	3 Br_2
5–7	p–chlorophenol	"	100	30	2 "
5–7	o–nitrophenol	"	50	30	2 "
5–6	m–nitrophenol	"	50	5–30	3 "
7–9	p–nitrophenol	"	50	5–30	2 "
15–18	2, 4–dinitrophenol	"	50	30	1 "
5–6	salicylic acid	"	50	30	3 "
5–6	m-hydroxybenzoic acid	"	50	15	3 "
6	methyl salicylate	"	50	30	3 "
4–5	phenyl salicylate	"	50	30	6 "
6–7	acetyl salicylic acid	"	50	30	3 "
5–6	m–cresol	"	50	1	3 "
5–6	resorcin	H_2O	100	1	3 "
12–15	β–naphthol	NaOH	....	15–20	1 "
4–8	thymol	"	....	15–20	2 "
5–6	aniline	HCl	50	5–10	3 "
10–12	p–chloraniline	"	50	10	2 "
5–6	o–nitraniline	"	100	30	2 "
5–6	m–nitraniline	"	50	30	3 "
5–7	acetanilid	"	50	5–10	3 "
5–6	sulfanilic acid	NaOH	50	30	3 "
5–6	metanilic acid	"	50	5–15	3 "
5–6	anthranilic acid	"	50	30	3 "
5–6	m–aminobenzoic acid	"	50	10–15	3 "
5–6	m–toluidine	HCl	50	5–10	3 "

In certain cases, to which the excess method is not applicable, excellent results were obtained by Day and Taggart (132) by direct titration, using spot tests on potassium iodide-starch paper. Instances are ortho-cresol, ortho-toluidine and para-toluidine, each of which consumes 2 Br_2 per mole. The spot method of determining the end point was used previously by Reinhardt[30] in the determination of aniline and toluidine in the presence of each other.

o-(8)-Oxyquinoline, according to Berg (126), forms 5,7 dibrom-o-oxyquinoline when brominated:

$$C_9H_7ON + 2\,Br_2 = C_9H_5ONBr_2 + 2\,HBr.$$

About 0.1 g. of the sample is dissolved in 2 *N* hydrochloric acid, several drops of 1% indigo-carmine or, according to Kolthoff preferably of 0.2% alcoholic methyl red solution, are added and the titration with 0.1 *N* bromate-bromide solution carried to the point where the solution turns yellow. Several cc. more of the bromate solution are introduced, then potassium iodide and the final titration made with thiosulfate, with starch as indicator. The brown precipitate, an iodine addition product, which appears when the iodide is added, redissolves quickly during the titration with thiosulfate. One cc. of 0.1 *N* $KBrO_3$ solution corresponds to 3.63 mg. of o-oxyquinoline.

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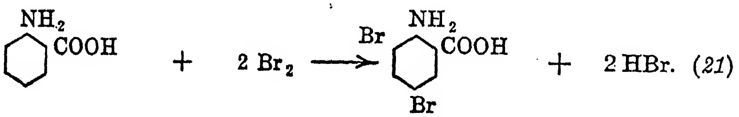
[30] Reinhardt, Chem. Zeit. *17*, 413 (1893).

Quinosol, $(C_9H_7ON)_2 . H_2SO_4 . K_2SO_4$, and superol $(C_9H_7NO)_2 . H_2SO_4$, can be assayed by this procedure.

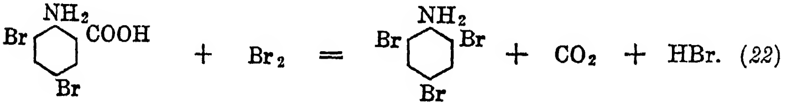
Fleck, Greenane and Ward (155) describe another method of titrating 8-oxyquinoline. Atanasiu and Velculescu (153) titrate potentiometrically with bromate-bromide solution.

Berg's method (125) has become of importance in the analysis of metals, since with o-oxyquinoline, a whole series of metal ions can be precipitated quantitatively and also separated from each other. The bromination procedure just described can be applied to these precipitates, giving a rapid method of determining these metals. Details are given in Berg's book.[81]

Anthranilic Acid, in conformity with Vaubel's rules (p. 111) gives on bromination, primarily di-bromanthranilic acid:



Only after an excess of bromine has been allowed to react for a long time is the carboxyl group also displaced with formation of tribromaniline. (Compare the table of Day and Taggart, p. 113.)



Funk and Ditt (144) find that it is simpler to use only the primary bromination for the determination of anthranilic acid. They also state that by means of reaction (*21*) it is easy to determine metals which have been precipitated as anthranilates. The precipitate is dissolved in 4 *N* hydrochloric acid, a few drops of indigo-carmine solution added and the solution titrated to a yellow with bromate-bromide. Potassium iodide and starch are added immediately, and the determination completed by titrating with thiosulfate. During the bromination, the acid concentration should not fall below 1.5 *N*. One cc. of 0.1 *N* $KBrO_3$ solution corresponds to 3.43 mg. of anthranilic acid, or if *b* cc. of 0.1 *N* bromate is consumed, to $\frac{b \times Me^{II}}{8 \times 10^4}$ g. of metal (Me^{II} = atomic weight of a divalent metal).

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[81] Berg, "Das o-Oxychinolin (Oxin)," Enke, Stuttgart, 1935.

Funk and Ditt (145, 146) quantitatively precipitate zinc, cadmium, copper, cobalt and nickel in neutral or quite weak acetic acid solution by means of a 3% solution of sodium anthranilate and determine the metals by bromination (copper excepted). The sensitivity of the precipitation is, for Zn, Cd, and Cu, 1:1,000,000, for Co, 1:800,000, and for nickel 1:445,000. According to Funk and Demmel (156) manganese can be determined by an analogous method, although its sensitivity of precipitation is only 1:30,000. Lead, for which the precipitation limit is 1:100,000 can, according to Funk and Römer (161), be precipitated from a neutral, but not from an acetate solution, and determined by bromination.

Furfurol. According to Pervier and Gortner (114) the aqueous solution of 0.1–0.2 g. of furfurol is treated with 20% potassium bromide solution, using 5 cc. for each 100 cc. of the solution of the sample. The acid content is then brought to 4% by weight with hydrochloric or sulfuric acid. Then 0.1 *N* bromate solution is added slowly from a burette, with constant stirring, until a light yellow appears. This color soon fades. The end point is determined potentiometrically. One cc. of 0.1 *N* $KBrO_3$ solution corresponds to 0.004803 g. of furfurol. However, the bromine consumption depends on the temperature. Magistad (148) states that the potentiometric determination of furfurol in alcoholic solution at 18° C. with potassium bromide-bromate, gives values agreeing with theory. Sasaki (137) studied the influence of temperature on the bromination of furfurol over the range 15–35° C., and gives a table showing the volume (in cc.) of 0.02 *N* bromate consumed by 1 mg. of furfurol in this temperature range, for instance, 2.122 cc. at 20° C. Hughes and Acree (157) treat furfurol at 0° C. for 5 minutes with an excess of 0.1 *N* $KBrO_3 + KBr$ in 3% hydrochloric acid and after adding potassium iodide and starch, titrate back with thiosulfate. The equivalence ratio agrees with the theoretical (1 mole of furfurol consumes 1 mole of bromate) so that here also 1 cc. of 0.1 *N* $KBrO_3$ solution indicates 0.004803 g. of furfurol.

MANCHOT'S BROMOMETRIC METHOD

The basis of bromometry as developed by Manchot (168-177) is the titration of free bromine with arsenious acid. This principle may be applied to every reaction producing or consuming bromine, in so far as it proceeds quantitatively and if special difficulties do not arise in individual cases. In strong hydrochloric acid solution the determinations involving consumption of bromine may also be accomplished with bromate. However, free bromine usually works more smoothly and gives sharper end points. Bromine solution, however, can not be replaced by bromate at all in the range from alkaline to weakly acid.

Arsenic trioxide serves as primary standard. It is easily prepared, in the requisite degree of purity, by sublimation in dry carbon dioxide. Solutions of 0.1 *N* As_2O_3 in alkali bicarbonate or hydrochloric acid are used. To prepare the hydrochloric acid solution, the arsenious acid is dissolved in sodium hydroxide, and treated with sufficient hydrochloric acid to make the standard solution about 0.2 *N* with respect to this acid. The bromine solutions may be one of the following:

1. Aqueous bromine solutions, which because they are very unstable. can be used only at a maximum concentration 1/30 *N*;

2. The more stable 0.1 *N* bromine solutions in 20–22% hydrochloric acid or in 1 *N* potassium bromide solution;

3. Glacial acetic acid solutions of bromine that are used for the determination of the iodine-bromine number.

The tension of the bromine vapor above the bromine solutions, decreases in the order just given (173), that is, it is least above the glacial acetic acid solutions which, therefore, are the most stable. This assumes that they contain no formate. (Formate-free glacial acetic acid can be prepared by distillation over pulverized potassium permanganate). The strength of the bromine solutions must be determined from time to time against the arsenite solution, whose strength remains constant. Hypobromite solutions are also used. These are prepared by treating a known volume of 0.1–0.2 *N* bromine solution in 1 *N* potassium bromide with considerably more than double the required amount of 0.5 *N* sodium hydroxide solution.

A solution of indigo carmine (0.2%) serves as indicator. With colored solutions, such as chromic and ferric, mixtures of 0.2 g. of indigo carmine and 0.2 g. of styphnic acid (trinitro-resorcinol) dissolved in 100 cc. of water have proved better. The color change is usually indistinct in such colored solutions and the supplementary yellow provided by the nitrated resorcinol makes this change easier to detect. It is better to add the indicator only toward the end of the titration. With a final volume of 80 cc., 3 drops of indicator will suffice and, on an average, this will consume 0.05 cc. of 0.1 *N* bromine solution. This may be included in the calculation.

Manchot and Oberhauser (172) after an extensive study of the equilibrium relationships of the fundamental titration of arsenious acid with bromine solution, found that 24% hydrochloric acid represents the maximum permissible acid concentration at the end point of the titration. Below this upper limit a system will never arise in which the bromine consumption of the arsenious acid will be incomplete, even though potassium bromide is added in the course of the various operations.

The chief source of error in these titrations is the volatility of the bromine. The following precautions provide sufficient protection against this: Wherever possible, the bromine solution is run into the other solution, the titration is made in small, stopper flasks with rather narrow openings, and hydrochloric acid or, in certain cases, potassium bromide also is added beforehand to the reaction mixture in which bromine appears. In addition, the bulk of the bromine is removed by excess arsenious acid and the back-titration is made with bromine.

PARTICULAR DETERMINATIONS

Antimony and Tin. Manchot and Oberhauser (173) found when titrating antimonous salt that it is advisable to add excess bromine and then titrate back since, in the last stages, the oxidation does not occur instantaneously. The titration of stannous solution should be made in the same way in order to obviate, as much as possible, the co-action of the atmospheric oxygen.

Iron. According to Manchot and Oberhauser (176) the iron is reduced with sulfurous acid or electrolytic cadmium. The acid ferrous solution is then treated with about 1 g. of potassium fluoride and 20 cc. of approximately 15% hydrochloric or sulfuric acid. An excess of 0.1 *N* bromine solution in 1 *N* potassium bromide is added and, after standing 1–2 minutes, the back-titration is made with arsenious acid. Phosphoric acid may be substituted for the potassium fluoride, enough being added so that the solution contains about 2–10% H_3PO_4. If the concentration exceeds 15%, the indicator change is retarded.

Chloride of Lime, Sodium Hypochlorite, Chlorine Water. The solution of the sample is run into a mixture of 30 cc. of 0.2 *N* potassium bromide and 30 cc. of 15% hydrochloric acid, and then titrated with 0.1 *N* arsenious acid [Manchot and Oberhauser (168)]. The solution of these materials may be introduced also into weakly alkaline arsenious oxide, acidified and then titrated back with bromine solution. Chlorates do not interfere when this latter procedure is used.

Pyrolusite, Lead Dioxide, Bichromate, Permanganate. Manchot and Oberhauser (168, 173) direct that the sample be heated with hydrochloric acid, and the resultant chlorine passed into acidified potassium bromide. Three receivers joined in series are necessary. In some cases arrangements for cooling should be made. The expulsion of the chlorine is hastened by means of a slow stream of carbon dioxide. It is somewhat simpler to add the sample to a strongly acid solution of arsenious oxide that contains 1 g. of potassium bromide (30–40 cc. of concentrated hydrochloric acid should be used). The back-titration is made with bromine solution. When assaying pyrolusite and lead dioxide, the system is warmed to 50–70° C. until the decomposition is complete, and then back-titrated.

Ozone. [Manchot and Oberhauser (169)]. An adequate volume of a solution of 2.5 g. of potassium bromide in 100 cc. of 2–5 *N* hydrochloric acid is forced into the gas burette containing the ozone. The contents of the burette are rinsed with the same reagent into a measured volume of 0.1 *N* arsenious acid solution, and the excess titrated with 0.1 *N* bromine solution. The method was tested on gas mixtures that contained 10% ozone. One cc. of 0.1 *N* As_2O_3 solution corresponds to 1.12 cc. of ozone, measured under standard conditions.

Sulfurous Acid, Hydrogen Sulfide and Thiosulfate. [Manchot and Oberhauser (170)]. The solution of the sulfur dioxide is run beneath the surface of a hydrochloric acid solution of bromine to prevent loss by volatilization and also to avoid oxidation by the air. The back-titration is made with arsenious acid. This method is not limited in its application to a narrow range of concentrations. The determination of hydrogen sulfide, whose solution is added to an excess of bromine dissolved in hydrochloric acid, is made in the same way. In both instances the oxidation proceeds smoothly to sulfate. According to Manchot and Oberhauser (173), it is better to brominate thiosulfate with alkaline bromine solution. This method may be applied also to sulfide and sulfurous acid. In this case, too, these materials must be brought below the surface of the hypobromite solution.

Phosphorous and Hypophosphorous Acids. [Manchot and Steinhäuser (171)]. The phosphite solution, if acid, is neutralized with sodium bicarbonate and then an excess (2–3 g.) of this salt or of sodium acetate is added. Bromine-potassium bromide solution is run in until a yellow color appears. This is discharged with arsenious acid, the indicator added, and the final titration made with bromine. The hypophosphite solution is treated in a flask with sodium acetate and bromine solution in excess, allowed to stand closed for 30 minutes, warmed, but not above 60° C., and after cooling, is titrated back with arsenious acid.

In order to determine phosphite and hypophosphite in the presence of each other, their sum is determined bromometrically, using the procedure given for hypophosphite. In a second sample, after complete oxidation with bromine, the phosphate is determined gravimetrically. Any phosphate that was present originally must be determined gravimetrically beforehand, and deducted.[32]

Nitrite. [Manchot and Oberhauser (173)]. The nitrite solution is allowed to react for about 5 minutes in a closed vessel with sodium bicarbonate and bromine-potassium bromide solution. The bromine excess is removed with an alkaline solution of arsenic trioxide, the solution is acidified and then titrated with bromine.

Ammonia. [Manchot and Oberhauser (164)]. The ammonium salt is added to 0.1–0.2 N hypobromite solution and swirled several times. After 1–2 minutes, the solution is acidified with hydrochloric acid, and titrated back with arsenious acid. The method gives values with ammonium chloride, sulfate, and nitrate which agree well with the acidimetric determinations. Kolthoff and Laur [33] found that when ammonia is oxidized by hypobromite, small quantities of nitric oxide are always produced along with nitrogen. The accurate results obtained by Manchot's method are due, possibly, to a compensation of errors.

Urea. [Manchot and Oberhauser (173)]. The procedure is that for ammonia, but the acidification is made only after 15 minutes. The method gives correct results when applied to pure urea solutions.[34]

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[32] The iodometric method of Wolf and Jung is simpler, Z. anorg. Chem. *201*, 337 (1931).

[33] Kolthoff and Laur, Z. anal. Chem. *73*, 177 (1927). Compare Artmann and Skrabal, Z. anal. Chem. *46*, 5 (1907), van der Meulen, Chem. Weekblad *27*, 551 (1930).

[34] Compare van der Meulen, Chem. Weekblad *27*, 551 (1930).

Hydrogen Peroxide. [Manchot and Oberhauser (173)]. The hydrogen peroxide solution is run into an excess of hypobromite solution, swirled, acidified and titrated back with As_2O_3.

Thiocyanate, Cyanide, Ferrocyanide. [Oberhauser (175)]. The sulfuric acid solution of thiocyanate is treated with 0.1 *N* bromine solution until a distinct yellow appears. After standing 10 minutes in the stoppered flask, the solution is treated with excess 0.1 *N* arsenious acid, several drops of indicator added, and the titration made with bromine. Cyanide may be determined in the same way. Ferrocyanide may be titrated also by this procedure, only the bromine excess must be reduced immediately with arsenious acid to prevent bromination of the cyanide groups. The equivalence relationships may be deduced from the following equations:

$$CNS^- + 4\,Br_2 + 4\,H_2O = BrCN + SO_4^{--} + 7\,Br^- + 8\,H^+$$

$$HCN + Br_2 = BrCN + H^+ + Br^-$$

$$2\,Fe(CN)_6^{----} + Br_2 = 2\,Fe(CN)_6^{---} + 2\,Br^-.$$

Formic Acid. In neutral solution, bromine oxidizes formic acid:

$$HCOOH + Br_2 = CO_2 + 2\,H^+ + 2\,Br^-.$$

A comparatively rapid reaction is obtained by utilizing the buffer action of sodium acetate. According to Oberhauser and Hensinger (177), the sample is treated, in a stopper flask, with 10 cc. of saturated sodium bicarbonate or acetate and excess bromine-potassium bromide solution. After 15 minutes, 0.1 *N* arsenious acid is run in until the color is discharged. The solution is titrated then with bromine to a sharp end point, using indigo carmine as indicator.

Organic Addition and Substitution Reactions. These may be carried out [Manchot and Oberhauser (170, 174)] just as well with bromine solution as with bromate-bromide solution. Nothing more need be said here on this subject since it was taken up under the bromate methods except to point out that Pamfilov and Kisseleva[35] found that aniline can be titrated directly with bromine, using indigo carmine as indicator. This had been brought out many years before by François.[36]

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[35] Pamfilov and Kisseleva, Z. anal. Chem. *72*, 100 (1927); *75*, 87 (1928).

[36] François, J. pharm. chim. *9*, 521 (1899).

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PART V

CHROMOUS SOLUTIONS AS VOLUMETRIC REDUCING AGENTS

BY

ERNA BRENNECKE

CHROMOUS SOLUTIONS AS VOLUMETRIC REDUCING AGENTS

As EARLY as 1922, Dimroth and Frister (6) used chromous chloride solution for titrating γ,γ'-dipyridyl and recommended it as "a very convenient reducing agent, well suited for titration and scarcely changing its titer with time," provided that it is properly stored and used. Later, Buehrer and Schupp (7) published experiments in which chromous solution was used directly as standard titrating liquid for (potentiometric) determinations.

Müller (23) and Someya (24) determined chromous salt, and chromium in general, by treating chromous salt with an oxidizing agent. This had previously been suggested by Zimmerman [(25) p. 322].

Someya attempted to also determine chlorate and nitro-compounds by reducing them with an excess of chromous chloride, titrating back with a ferric solution, using thiocyanate as indicator. Buehrer and Schupp consider this the most practical method of using chromous chloride solution.

Zintl and his various collaborators in 1927 began to publish a series of studies of the use of chromous solutions for the direct potentiometric titration of single heavy metals and of several metals in the presence of each other (9, 10, 13, 15, 16). These procedures were based essentially on experiences with titanous chloride solutions. Subsequently, Brintzinger and his co-workers made an extended study of the potentiometric application of chromous salts (11, 12, 17, 18, 19).

General Considerations

Characteristic Properties of Chromous Solutions. The significance of chromous solutions for volumetric analysis lies in their high reducing power, which is considerably greater than that of titanous chloride solutions. For purposes of comparison, the normal potentials (referred to *N* hydrogen = 0) of several strong reducing agents are given:[1]

Lower Stage of Oxidation	Higher Stage of Oxidation	E_{0_H}
Zn	Zn^{++}	—0.76 volt
Fe	Fe^{++}	—0.44
Cr^{++}	Cr^{+++}	—0.41
Cd	Cd^{++}	—0.40
Ti^{+++}	Ti^{++++}	—0.04
Sn^{++}	Sn^{++++}	+0.2
Fe^{++}	Fe^{+++}	+0.75

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[1] According to Kremann and Müller [(30) page 786].

It should be noted that the values for reduction-oxidation equilibria based on the discharge of ions are not strictly accurate and consequently cannot be used in calculating the end point potentials that are so important in titrations. This is because the interionic forces make themselves quite evident in the case of multivalent ions at higher concentrations and in the presence of other electrolytes. Furthermore—especially with halides—the formation of complex compounds must be taken into consideration and in certain cases, such as titanic salts, hydrolysis plays a part. The extent to which the volumetric application of chromous solutions is affected through the displacement of the reduction-oxidation potentials by these factors is shown in the Special Section (p. 139). Grube and Schlecht (1) found that the value determined for the potential corresponding to the reaction $Cr^{++} \rightarrow Cr^{+++}$ is quite dependent on the electrode material, on the anion of the salt, on the total chromium content of the solution and on the quantity of acid present. In particular, if the normality of the acid is doubled, the potential becomes more noble by several hundredths of a volt. Jablcznski (2) and Asmanow (3) found that the acid and the chloride concentration exert a marked influence on the behavior of chromous solutions.

Zintl and Rienäcker (9) state that the titration range in 5% HCl is increased by about 300 millivolts with chromous solution as compared with titanous chloride. This corresponds almost to the difference in the normal potentials given above. Consequently, the scope of its use is greater. They found furthermore that chromous solutions usually react more rapidly than titanous solutions.

One consequence of the strong reducing character of chromous solutions is that they are *very sensitive to air.* It is necessary, therefore, to prepare and store chromous solutions with particular care and when titrating to prevent, so far as possible, any contact with atmospheric oxygen. Zintl and his co-workers use equipment which is quite suitable for practical purposes (see p. 136).

Another characteristic property of chromous solutions is obviously of considerable importance to their use in volumetric determinations. Since the normal potential of the system Cr^{++}/Cr^{+++} is about 0.4 volt below that of the normal potential of hydrogen, *an acid chromous solution, at least, must set hydrogen free.* However, Döring (4), Traube, Burmeister and Stahn (5) and Asmanow (3) proved that this reaction occurs to only a slight extent unless catalytically active materials such as platinum, finely divided gold and, above all, palladium are present. Döring states that certain forms of silicic acid also accelerate this reaction; Traube, Burmeister and Stahn found that arsenic sulfide and also antimony sulfide have this same effect. Only a minimal liberation of hydrogen was observed by Döring in an approximately 0.04 *M* $CrCl_2$ solution that was about 1.4 *N* with respect to HCl, even when it was heated to incipient boiling. Asmanow carried out experiments (also in the absence of platinum) at various temperatures and acid concentrations. He obtained a noticeable decomposition in 2 *N* hydrochloric acid at 30° C. with 0.03 *M* chromous sulfate; in 4 *N* hydrochloric acid, 1.6 cc. of hydrogen was generated in 15 minutes. In contrast, no hydrogen was produced in 4 *N* sulfuric acid. Asmanow found the same decomposition velocity in 1 *N* as in 5 *N* hydrochloric acid, when the solution was made 5.4 *N* with respect to ammonium chloride. In this connection compare also (2).

These observations indicate that the *purest materials* are necessary for the preparation of a solution that will be reliable and *stable.* Chromous solutions are better than titanous solutions because they can be prepared more easily in the requisite degree of purity, so that apart from catalytic decomposition of the solution, the difficulties encountered with iron-bearing titanous solutions can be avoided, even in the titration.

Even though an adequate stability of very weakly acid chromous solutions is thus assured (see also p. 135) *the ease with which the reaction between chromous ions and hydrogen ions occurs* must not be disregarded in titrations in which finely divided metal is set free. Obviously this is the explanation for many differences in the findings (see p. 143).

The Preparation and Stability of Chromous Solutions. Dimroth and Frister (6) dissolved crystallized chromous chloride in water that had been boiled and then saturated with carbon dioxide.

Traube, Burmeister and Stahn (5) as well as Asmanow (3) reduced chromic salts electrolytically and prepared the chromous salt from the material thus obtained.[2] The former make use both of the low solubility of organic chromous salts and their comparatively great stability in air, while the latter worker precipitates the purest possible $CrSO_4.5H_2O$ with alcohol and so obtains a material that is quite stable if it is well dried and shielded from moisture. Grube and Schlecht (1) also obtained their chromous solutions electrolytically.

Buehrer and Schupp (7) prepare the chromous chloride solution by the procedure that is also preferred by Zintl. Potassium bichromate and concentrated hydrochloric acid are heated together and the resulting chromic chloride solution is reduced with zinc that contains no arsenic or iron. They do not remove the zinc chloride, and shield the solution from air by overlaying it with kerosene, a device that assuredly is rather questionable in volumetric analysis.

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[2] See Foerster, [(31) p. 602].

Thornton and Sadusk (20) prepared a very stable solution containing little zinc by slowly passing a sulfuric acid solution of bichromate through a column of amalgamated zinc.

The following method of preparation has been tested by Zintl and Rienäcker (8, 9) and is essentially that also adopted by Brintzinger (12). Pure, recrystallized potassium dichromate is heated with concentrated hydrochloric acid,, cautiously at first, then more intensely until the evolution of chlorine ceases. An excess of pure zinc is introduced and the solution allowed to stand until it acquires a pure blue color, indicating that all the chromium is present in the divalent state. This reduction requires several hours. During this period the flask is closed with a two hole stopper, one opening carrying a short tube with a Bunsen valve, the other a second tube extending to the bottom of the flask and closed at first with a pinch clamp.[3] The chromous solution is then blown through a glass wool filter into a flask filled with an indifferent gas (pure carbon dioxide washed with chromous chloride is most convenient) and containing boiled, concentrated sodium acetate solution. The transfer into the second flask is made with hydrogen (Kipp) that has been freed of oxygen by means of a chromous chloride solution prepared by reducing potassium bichromate with zinc and hydrochloric acid. Slightly soluble, red chromous acetate precipitates at once. It settles well. There must be so much sodium acetate present that the supernatant liquid is no longer blue. The flask (Rienäcker uses a large bottle) should have a wide neck, fitted with a three or four hole stopper. These openings carry glass tubes: (1) for the intake of the chromous solution or for the admittance of the hydrogen (2), for the wash water (3), for siphoning off the solution (4), for the escape of the hydrogen when water is added.

The liquid standing over the chromous acetate is blown off by hydrogen under pressure. Then the precipitate is washed repeatedly by decantation with water that has been boiled and allowed to cool under carbon dioxide. According to Rienäcker, 7–10 washings with fresh water are enough for the preparation of chromous chloride solutions. However, since the efficiency of the washing depends on the quantities of materials involved and on the volume of water added each time, it is better to test the progress of the washing, from time to time, with silver nitrate (for chloride) or with hydrogen sulfide (for zinc). Before testing with silver nitrate the chromous salt must be removed by warming for a short time with a little dilute nitric acid. Sodium acetate should be added before testing with hydrogen sulfide. The chromous acetate is dissolved in air-free 2% hydrochloric acid; about 730 cc. is required for 2 liters of 0.1 *N* chromous solution. To avoid too great an excess of the acid, only so much is added that a small amount of the salt remains undissolved. The blue solution is blown by means of hydrogen or carbon dioxide into the storage vessel (see below) that has been filled with an indifferent gas (carbon dioxide is best). Any small particles of chromous acetate that may have been carried over are dissolved by adding a few cubic centimeters of hydrochloric acid. The solution is made up to the desired volume with boiled water.

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[3] It is best to use cork stoppers made impermeable (with picein, for example) rather than rubber stoppers, because there is danger that the latter may introduce hydrogen sulfide into the solution. In preparing the chromous solution and when transferring it, greased glass cocks should be avoided so as to keep the burettes as clean as possible. Glass to glass connections joined by short lengths of rubber tubing that have been boiled in hydrochloric acid are better.

Chromous sulfate solution is prepared from chromous acetate in the same way. In this case the chromous acetate must be washed until the chloride has been reduced to the minimum. As will be seen in the Special Section, it is by no means immaterial whether titrations with chromous solutions are carried out in the presence of chloride or sulfate. Chromous sulfate solution is decidedly preferable to the chloride solution because of its more general applicability [compare (32) p. 458].

A chromous chloride or sulfate solution, prepared as described, will, if properly stored (see below) have a practically constant titer for at least eight days. Zintl and Rienäcker, however, caution against shaking the solution after it has been standardized. They also advise against using the solution to the very end. Rienäcker found that 25 cc. of copper sulfate solution consumed, after the stated number of days, the following volumes of chromous chloride:

Days	0	1	4	6	12	15
cc. $CrCl_2$	16.11	16.11	16.12	16.12	16.14	16.14

Consequently, it is sufficient to check the titer every few days.

When Rienäcker did not purify the chromous salt through the acetate, the solution was much less stable; the titer decreased about 4% in six days.

Brintzinger and Rodis recommend that the precipitated chromous acetate be purified not by decantation but by filtering it, in an atmosphere of carbon dioxide, on a Buchner funnel and washing thoroughly with boiled water. They obtained a very stable solution.

figures on which the recalculation was based are given in the following Table:

ELECTRODE	VOLT
Hg/Hg_2SO_4, 1 *N* H_2SO_4 ,	+0.692*
Hg/Hg_2SO_4, 2 *N* H_2SO_4 ,	+0.676†
Hg/Hg_2Cl_2, 1 *N* KCl	+0.284
Hg/Hg_2Cl_2, sat. KCl	−0.249‡
Normal hydrogen electrode	0.000

* Ostwald-Luther, "Physiko-chemische Messungen," Leipsic, 1910, p. 445.

† Zintl, Berl-Lunge [(32) p. 439].

‡ Zintl and Reinäcker (8, 9) after Michaelis, "Die Wasserstoffionenkonzentration," Berlin, 1914.

Finally, certain fundamentals concerning the *performance of the titration* must be given:

If correct results are to be obtained, the solution to be titrated and the space above it, which always contain air, must first be freed of oxygen. It is customery to *boil the solution in the titration vessel for several minutes while carbon dioxide is passed through.* If the reduction with chromous salt produces a material that is oxidized easily by free oxygen (cuprous or ferrous salt) it is simpler to use the "pre-reduction" proposed by Zintl and his collaborators. In this, a small part of the material being determined is reduced first with chromous solution. The reduction product is then partially re-oxidized by the dissolved oxygen and the remainder is transformed completely to its original state by another oxidizing agent. It is sufficient for this pre-reduction to add about 5 cc. of chromous solution to the hot solution covered with carbon dioxide. After several minutes, the reduction product has consumed the oxygen present, and the material to be titrated can then be reoxidized completely, under potentiometric control, with a suitable oxidizing agent (bromate, dichromate or permanganate solution). A slight excess of the oxidizing agent will not interfere at all, because it is removed by the chromous solution at the beginning of the titration. The first break in the potential is taken, of course, as the null point of the titration.

Nitrate ion interferes in titrations with chromous solutions and must be previously removed.

The Standardization of Chromous Solutions. Zintl, and later Brintzinger also, determined the strength of *chromous chloride* solutions by titrating a hydrochloric acid solution of purest (particularly iron-free) *copper sulfate.* The writer has confirmed the reliability and convenience of this standardization. Buehrer and Schupp recommend *potassium bichromate* as primary standard.

Chromous sulfate can likewise be standardized against *copper sulfate,* but it should be noted that in a solution containing sulfuric acid alone, copper sulfate is reduced to metal before the jump in the potential occurs, while in the presence of sufficient hydrochloric acid the reduction proceeds only to univalent copper. Both procedures give concordant results. Details of the copper titration will be given presently.

Potassium bichromate is also an excellent standard for chromous sulfate solutions. In this case, the potentials are established somewhat more slowly than in the copper titration. The writer has found that the titer obtained against these two standards differs on the average 0.15%. For details see p. 146.

Special Section

Determination of Copper. The composition of the copper solution plays an important rôle in the reaction between cupric and chromous ions.

a. Titration in hot (about 80° C.) *hydrochloric acid solution* (8, 9) leads to a smooth *reduction to cuprous salt.* Rienäcker observed that the result is the same for hydrochloric acid concentrations between 2 and 20%. He usually used 5% HCl. The writer's own experiments, carried out under these latter conditions, confirmed the accuracy of this determination. The establishment of the potential is excellent, the potential break is sharp (about 0.3 volt for one drop of 0.1 N chromous solution). The end point potential lies at $E_H \backsim +0.17$ volt.[4]

In this case, at the beginning of the titration, the solution can be freed of air, either by boiling or by "pre-reduction." If the latter procedure is followed and potassium bromate solution is used for the oxidation, the first jump, indicating the beginning of the reduction of the cupric ion, occurs at about $E_H \backsim +0.85$ volt. After the cuprous salt has been quantitatively formed, it is reduced to metallic copper by further addition of chromous chloride or sulfate solution. However, in the hydrochloric acid concentrations given above, the reaction is not quantitative

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[4] In order to arrive at this value referred to the normal hydrogen electrode, there is added, for instance, to the potential (= —0.52) measured against the 1 N sulfuric acid-mercurous sulfate electrode, the difference in potential between the mercurous sulfate—and the normal hydrogen electrode:

$$-0.52 + 0.69 = +0.17.$$

Apparatus and Procedure. When working with solutions that are as sensitive to air as chromous solutions, it is necessary to use suitable and convenient apparatus. The equipment described by Zintl and Rienäcker is particularly good (26, see also 8, 9):

The essential parts of the storage vessel are shown in Fig. 1, but the position of the side tube A is somewhat different from that given by Zintl and Rienäcker. It is better to have this at the head of the stopper rather than directly below the cock H_2, so that when the solution is run in the gas can escape more easily from the bottle, and the solution does not come in contact with the cock H_2, where it might be contaminated with stopcock grease. The solution is always kept under hydrogen, drawn from a Kipp apparatus. The gas, washed by passing it through a bottle containing alkaline permanganate solution and through two bottles charged with chromous chloride solution, enters at A. It is not advisable to use carbon dioxide because supersaturation of the solution can easily cause the formation of bubbles in the outlet tube of the burette (27).

The titration is made in a beaker closed with a rubber dental dam, that should be boiled in dilute hydrochloric acid before being used. A 400 cc. beaker of the tall type is best because about 200 cc. is the usual volume of the solution. The necessary openings are made in the rubber cap with a sharp cork borer: one larger opening fitted with a short tube that serves as a guide for the stirrer and also for the escape of the steam, and four small openings for: the auxiliary electrode, the burette tip, the gas lead-in tube with the electrode, the addition of the oxidizing agent required in the pre-reduction (see p. 138). The latter opening can also be used for determining the temperature at the end of the titration; when not in use it should be closed in some suitable way. The wider exit tube serves also, as Zintl proposed, for catching the steam condensate; for this purpose it is inserted into the opening of a short, medium sized rubber stopper pushed into a glass cup, about two centimeters high and several centimeters wide (compare Fig. 2).

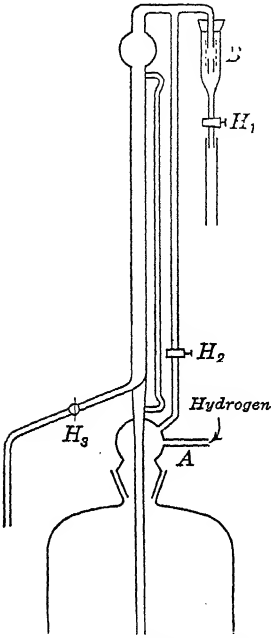

Fig. 1 B = Bunsen valve; H_1, H_2, H_3 = glass cocks. (The burette attachment with H_3 in reality is turned 90° toward the front). The side arm A serves for introducing the solution or hydrogen. The burette is filled by suction at H_1, H_2 is closed during this operation.

The platinum wire, several centimeters long, that serves as the *indicator electrode* must not be too heavy, since in titrations during which metal is deposited, it is necessary to allow the stirrer to rub against the electrode so that the continuous jarring will keep the electrode from becoming heavily coated with metal. A satisfactory establishment of the potential requires that the wire be cleaned before every titration with hot chromic-sulfuric acid, washed thoroughly and then ignited. Any adhering metals are removed beforehand with concentrated nitric acid. Zintl recommends that the electrode be rubbed off occasionally with fine emery paper.

Carbon dioxide is best for *excluding the air* during the titration; it is drawn from a cylinder and washed with chromous chloride solution. In titrations in which air-sensitive materials, such as cuprous salts, are formed, it is particularly important to keep out all oxygen and so the carbon dioxide must be thoroughly washed, even though a heavy current of this gas is swept through the solution being titrated. This washing is accomplished by passing the carbon dioxide through chromous chloride solution contained in two or three wash bottles fitted with fritted glass diaphragms, which divide the gas into very fine bubbles. Kolthoff (33) recommends that an additional ordinary wash bottle containing water be inserted in front of the titration vessel to protect the chromous chloride solution in the other wash bottles.

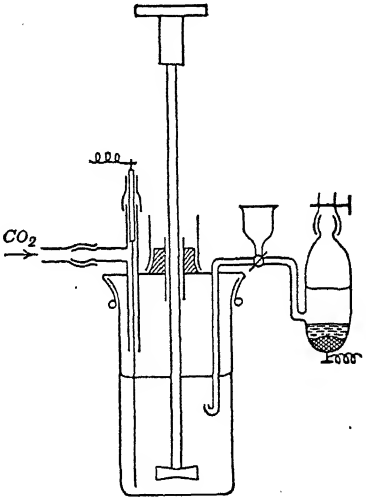

FIG. 2

The *potential can be measured* by one of the usual methods. Zintl used for the *reference electrode* either a calomel electrode filled with saturated potassium chloride solution or a mercurous sulfate electrode with 2 N sulfuric acid. The connecting vessel contained the same solution as the electrode. Brintzinger also used a saturated calomel electrode. The writer used a mercurous sulfate electrode with 1 N sulfuric acid, with saturated potassium sulfate solution as the intermediate liquid. *The end point potentials given in the Special Section have all been recalculated to the normal hydrogen electrode as null value,* disregarding the liquid potentials, in order to make a comparison of the values easy. The (see also below) because much of the cuprous chloride is bound into complexes.

b. If the reduction of the divalent copper is carried out at 80° C. in *acetic acid* solution (8, 9) metallic copper separates at once. The establishment of the potential is slow and of no value. On the other hand, Rienäcker obtained, as in hydrochloric acid solution, a distinct break at the completion of the change of cupric to cuprous ion, if he added *sufficient sodium chloride or ammonium chloride* to the solution. The amount of chloride added can be varied considerably, but it must not be too little; for instance, about 10 g. may be present in 200–400 cc. The chloride forms a complex salt with the cuprous salt and thus facilitates its production. The end point potential lies at $E_H \backsim +0.13$ volt. In this case the oxygen is removed by boiling the solution; "pre-reduction" is not successful.

c. *The reduction of divalent copper to the metal* can be made the basis of an exact titration, if a *chloride-free sulfuric acid* solution is titrated with *chromous sulfate* (14,16). Metallic copper is not formed immediately in a hot solution but the initial product is cuprous sulfate. This, however, quickly goes over into copper and cupric sulfate. The break at the end of the reaction is very sharp (about 0.15 volt for one drop of 0.1 *N* chromous sulfate solution); according to Schloffer its position is somewhat dependent on the sulfuric acid concentration; in 5% H_2SO_4 it occurs at $E_H \backsim +0.06$ volt; in 10–20% at $E_H \backsim +0.14$ volt. The sulfuric acid concentration should, if possible, vary only between 2 and 15%, because in this range and with a titration temperature of about 80° C., the potential is established quickly. This is not true at higher or lower acid concentrations. Hölemann (21) observed that too much chromous sulfate solution is always consumed at high concentrations of sulfuric acid. *Atmospheric oxygen* can be removed by *"pre-reduction"* as when the titration is carried out in hydrochloric acid solution. Schloffer uses potassium permanganate or dichromate solution for the oxidation. The respective end point potentials indicating the beginning of the copper titration are: $E_H \backsim +0.92$ volt and $E_H \backsim +0.68$ volt.

The response of the platinum electrode is improved if it is placed so that the vanes of the stirrer will jar it. This prevents the formation of a heavy precipitate of metallic copper on the wire (see p. 137).

Even small quantities of *chloride* in the copper sulfate solution cause a transient precipitation of cuprous chloride, a slower adjustment of the potential and a blurring of the break. As the concentration of the chloride ion rises the formation of complex cuprous salts again plays a significant rôle. Schloffer recommends solutions that are either chloride-free or that contain at least 2% hydrochloric acid.

d. Rienäcker and Schloffer showed that these methods can also be applied extensively to solutions that contain other metals besides the copper.

Bismuth, mercury and silver, in hydrochloric acid solution, are reduced to the metal only *after* the cupric salt has been completely converted to cuprous salt. When mercury is present, there must of course, be enough chloride present to form the complex $HgCl_4^{--}$ ions, and thus impede the reduction of the mercury (see p. 142); otherwise the mercury will be titrated along with the copper. In these cases the potential at the end of the copper reduction lies at $E_H \sim + 0.25$ volt.

Gold, in hydrochloric acid solution, is reduced to metal even *before* the copper, provided that, because of high chloride ion concentration, the Au (III) is not bound too firmly as complex ion. In this case there is no distinct break between the gold and the copper reduction (see p. 150). In 2–5% hydrochloric acid, the copper begins to precipitate at $E_H \sim + 0.75$ volt.

In the presence of *trivalent arsenic,* copper can be determined in 5% hydrochloric acid, if the solution contains 10 g. of sodium chloride per 200–300 cc. *Quinquivalent arsenic* and also *tri- and quinquivalent antimony* are partially reduced along with the copper.

Rienäcker advises titrating copper in *acetate solution containing tartaric acid,* if *stannic* salt is present. The values are usually too high in hydrochloric acid solution.

Lead, cadmium, as well as those metals of the third group that are usually encountered, have no effect. *Iron,* on the other hand, *interferes,* since the iron reduction curve merges, with no break, into the copper reduction curve.

According to Schloffer, copper may be determined in *sulfuric acid solution* with no difficulty in the presence of *silver, iron, arsenic* (V), *lead, cobalt, nickel and aluminum. Trivalent arsenic* must be oxidized beforehand. In the presence of *antimony,* copper can be determined in sulfuric acid solution, if not more than 5 mg. of antimony is present per 200 cc. of solution. The writer has found that when *mercury* is present, two well defined jumps in potential occur in the determination of copper in sulfuric acid solution. In contrast to their behavior in solutions containing chloride, *silver and mercury* are reduced *before* the copper when *no chloride* ions are *present.* For additional information see p. 149.

Determination of Mercury. Rienäcker (8, 10) showed that mercury can be determined by means of chromous chloride in *acetic acid* and also in *hydrochloric acid* solution. Since the change from divalent to univalent mercury cannot be used for titration purposes and since because of its slight solubility mercurous chloride when once precipitated is reduced quite slowly by chromous solution, the titration must be made under conditions insuring the reduction of the mercuric salt directly to metallic mercury, without intermediate precipitation of mercurous chloride. This is accomplished by *adding enough chloride.* Mercuric chloride dissociates but slightly and correspondingly tends strongly to form complexes; the anion $HgCl_4^{--}$ is formed here and as this is quite stable, any calomel that has already precipitated dissolves with liberation of metallic mercury:

$$Hg_2Cl_2 + 2\ Cl^- = HgCl_4^{--} + Hg.$$

Under these conditions, a titration at about 80° C. gives a sharp break. In 3–5% hydrochloric acid this well marked jump (about 0.22 volt) lies at $E_H \backsim +\ 0.09$ volt; the writer found +0.19 volt.

Rienäcker observed that the results for 0.15–0.25 g. of mercury agree with the theoretical within 0.1–0.15%. If the solution contained more than 5% hydrochloric acid, or chloride in addition to 5% hydrochloric acid, or if the titration was made in acetic acid solution containing the large quantity of chloride essential to a smooth reduction,[5] then he found a decided increase in the volume of chromous chloride consumed. He was able to eliminate this over-consumption by adding *bismuth chloride,* which aided in the *transfer of charges.*[6] He obtained this same action with *copper or iron salt* in place of the bismuth chloride in hydrochloric acid solution, but not in acetic acid solution.

The writer could not confirm these favorable results of Rienäcker, even in titrations in 3–4% hydrochloric acid when no chloride was added. Neither could the effect of bismuth chloride be confirmed: without bismuth the over-values were as much as 3%; if 10, 20 or even 100 mg. of bismuth were present, the errors, always positive, still varied up to approximately 1.5%. The addition of 15 g. of ammonium chloride gave the same uncertain values.[7] In this study, the main portion of the chromous sulfate solution was always added rapidly, though in separate drops. In agreement with Rienäcker, the writer found that when bismuth chloride is present, the break is noticeably smaller (the writer found $\backsim 0.04$ volt) but is still detected easily: $E_H \backsim +0.20$ to $+0.10$ volt, depending on the chloride ion concentration.

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[5] Rienäcker ordinarily used 15 g. ammonium chloride per 200 cc.

[6] Rienäcker also observed over-consumptions, sometimes as much as several per cent, in the titrations of mercury with titanous chloride in acetic acid solutions containing ammonium chloride. The error was obviated by adding 5–10 cc. of 0.1 *N* bismuth chloride solution.

The *explanation* of these findings is to be sought naturally in the ease with which the following reaction takes place:

$$2\ \mathrm{Cr}^{++} + 2\ \mathrm{H}^{+} = 2\ \mathrm{Cr}^{+++} + \mathrm{H}_2.$$

Mercuric ions and chromous ions obviously do not react instantaneously with each other. Consequently, the solution temporarily contains a small number of chromous ions, which under the *catalytic influence of the finely divided metal*[8] or even of the platinum electrode[9] enter into reaction with the hydrogen ions.

If, in addition to the mercury, there is present in the solution a material which per se is *more difficult to reduce* (that is one which has a more negative reduction potential) than the mercuric ion, but which reacts *more quickly* with chromous salt than mercuric mercury, and whose reduction product reacts quantitatively and rapidly with mercuric ions (the material is thereby reoxidized, the mercury reduced) then the over-consumption, if due to the above reaction, will become less or entirely disappear since now there is less time available for reaction between chromous ions and hydrogen ions. Probably the bismuth chloride functions in this way, as is indicated by the lowering of the error from 3% to 1.5%. However, it does not react quickly enough with the chromous salt to entirely eliminate the error.

The rôle of the bismuth chloride can be taken over by *cupric salts;* the reduction of cupric to cuprous ion occurs quantitatively before the precipitation of the mercury, so that it ought not influence the mercury reduction; the reduction of cuprous salt to metallic copper occurs finally however only after the precipitation of the mercury. The effect of *iron salt,* that Rienäcker observed, cannot be explained in this wise because the change from ferric to ferrous ion is completed before the reduction of the mercury is finished.

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[7] Rienäcker, in a letter to the writer, surmised that the dissimilarity in our findings might be due to a difference in the condition of the platinum wires used by us. Compare the following discussion.

[8] See above, p. 132; especially Döring (4).

[9] See, above all, Grube and Schlecht (1).

Since mercuric ions are prone to form complexes in the presence of considerable quantities of hydrochloric acid or chlorides, the reduction to metallic mercury is correspondingly impeded, though as a consequence at the end of the titration, the mercury is much more finely divided than when ammonium chloride is absent. It is not surprising that, under these conditions, Rienäcker found that the over-values became larger, especially in view of the findings of Jablczynski (2) and Asmanow (3) who found that larger quantities of chloride accelerate the reaction between chromous chloride and hydrogen ions. Therefore it would seem *best to titrate in chloride-free mercuric sulfate solution* with *chromous sulfate.* Up to the present, the writer has been the only one to study this reaction. Her comparatively few trials were made in the presence of 3% sulfuric acid. These seem to confirm the above conclusion; the results conform to theory within 0.5%. Patently here also it is essential to titrate slowly. The potential break was very sharp ($\backsim$ 0.43 volt for 1 drop of 0.1 N ($CrSO_4$) and was found at $E_H \backsim + 0.33$ volt. Even in the *presence of copper sulfate* the jump amounted to 0.14 volt at a potential of $E_H \backsim + 0.52$ volt. A recognizable, but rather indistinct break occurs between the reduction to mercurous sulfate and that to metallic mercury.

Excess consumptions and their diminution or elimination by *charge carriers in titrations with chromous* (also *titanous*) solutions are not confined to the titration of mercury salts. On the contrary they are often found when metals are deposited during the titration. Examples are: gold (8, 15),[10] silver (8, 15), bismuth (14).[11] This matter will be further discussed in connection with the titration of silver.

It is evident then that mercury can be determined chromometrically, even though with no great accuracy. *Copper, bismuth and iron in hydrochloric acid* do not interfere. Since the cuprous or ferrous ions, produced before the precipitation of the mercury, consume the dissolved oxygen, the boiling of the solution may be omitted in these instances. In *acetic acid solution containing chloride, only bismuth may be present* along with the mercury, because copper and iron are "reduced, at least in part, along with the mercury" (10, 16).

According to Rienäcker, the titration may also be made if *gold* is present, because it is reduced before the mercury, even if the solution contains 15 g. of ammonium chloride. *Lead* and *cadmium* may also be present.

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[10] Ti (III): [(34) p. 221] (28); compare also [(34) p. 220] regarding similar observations during the titration of platinum.

[11] Ti (III): (29).

Quinquivalent arsenic, trivalent antimony, quadrivalent tin and *silver chloride* interfere. *Arsenic* (III) results in too high mercury values unless the chromous chloride solution is added drop-wise.

Determination of Silver. a. Silver sulfate, *in hot chloride-free sulfuric acid solution,* is reduced immediately to metallic silver by chromous sulfate. The potential adjustment is good and the break, which occurs at $E_H \sim +0.24$ volt amounts to about 0.36 volt for 1 drop of 0.1 N chromous sulfate solution.

Schloffer (14, 15) also obtained exact results that were independent of the sulfuric acid concentration, 2–20%. These findings are in contrast to those of the writer, who obtained *irregular over-consumptions* of as much as 1% in the presence of 1.6–5.6% sulfuric acid. On the average, the results were 0.5% in error, even when all the chromous sulfate solution was added drop by drop. A striking feature of the silver determination in the absence of other metals is that the potential always becomes more noble immediately after the break or within a few minutes. In one instance when there was considerable over-titration, an unmistakable evolution of gas was observed on the precipitated, spongy silver and on the platinum electrode. For the explanation of these observations see the discussion given under Mercury, p. 143. The results of the writer's attempts (see p. 146) to determine silver in strong hydrochloric acid containing much chloride, or in acetic acid solution, substantiate these views.

b. When silver is titrated in the *presence of chloride* (8, 15) the conditions are similar to those in the mercury titration. The reduction to metallic silver and the accompanying adjustment of potential is rapid enough only if the solubility of the silver chloride is increased by *adding a considerable quantity of alkali chloride or ammonium chloride.* If this is not adequate to dissolve all of the silver chloride by forming a complex with it, the titration must be conducted slowly near the end or else, after adding the main portion of the chromous solution, time must be allowed for the potential to reach a constant value.

Under these conditions, Rienäcker, who carried out the reduction in hot *hydrochloric acid solutions,* obtained values *several per cent too high* and varying with the chloride content. *Copper salts lowered the over-consumption* to 0.4–1%. He attained an *accuracy of 0.1%* when he treated the silver sulfate solution with 10–25 g. of ammonium chloride, 5 g. of *sodium acetate* and "several cubic centimeters of acetic acid." After diluting to about 200 cc. and boiling out the atmospheric oxygen, he titrated the hot solution with chromous chloride solution. The potential break was found at $E_H \sim -0.12$ volt.

The writer, like Rienäcker, obtained silver values several per cent too high in the presence of 15 g. of ammonium chloride and about 1% hydrochloric acid ($E_H \backsim +0.07$ volt). If instead of the latter acid, 2 cc. of glacial acetic acid was used, the results were still about 4% *too high* ($E_H \backsim -0.10$ volt). When 5 cc. of 2 *N* acetic acid was substituted for the glacial acetic acid, there was no definite break. Obviously in these cases, the silver reduction is impeded so much by the formation of the complexes (compare the decided shift of the potential to negative values) that the side reaction between chromous and hydrogen ion makes itself still more evident than in the titration of chloride-free solutions (see p. 143).

Rienäcker determined silver in the presence of *copper, gold, lead, tin (IV) and arsenic (III) in acetic acid solution containing chloride and acetate* (see p. 149 and p. 150).

Determination of Bichromate. The titration of bichromate is worthy of consideration particularly because, like copper sulfate, it is used for the *standardization of chromous sulfate solutions.*

Chromate can be titrated exactly with chromous sulfate at about 70° C. in 3–5% sulfuric acid. Using this acid concentration, Zintl and Zaimis (13) obtained excellent results at room temperature also. Care must be taken to *boil* the solution for *only a short time* when removing the atmospheric oxygen, or else some of the chromic acid will decompose. For this same reason, the solution should not contain more than 5% sulfuric acid. Hölemann (21) also found that the results are not reliable at higher acid concentrations. When less than 3% sulfuric acid is present, the establishment of the potential is too slow.

Under the conditions just outlined, the adjustment of the potential is distinctly slower than in the reduction of copper, for instance. This sluggishness can be ascribed to a lagging reaction between chromic acid and chromous sulfate. Hence it is advisable not to titrate too rapidly, and especially in the vicinity of the break to watch the potential for a short time after each addition of the titrant. After the first large break, another decided jump is often observed. The break is quite distinct:

0.55 volt, at $E_H \backsim +0.40$ volt. (In the presence of copper salt, the corresponding values are 0.1 volt and $E_H \backsim +0.60$ volt.)

The writer standardized chromous sulfate solution against purest $CuSO_4.5\,H_2O$ and $K_2Cr_2O_7$ and obtained an average agreement within 0.15%. The bichromate values were always somewhat the higher.

The bichromate titration does *not* seem to be *as suitable* for the *stand-*

ardization of chromous chloride solutions and the results repeatedly exhibit striking differences.

According to Zintl and Zaimis, the procedure just given permits the accurate titration of chromate, even in the *presence of iron.*

Vanadic acid, which is similar to chromic acid, can be determined by the same general procedure. The titration differs from that of chromate only in that the vanadium reduction curve shows two breaks: the first after the complete change into vanadyl salt and second after reduction to trivalent vanadium. See Zintl and Zaimis (13) for details.

Determination of Tin. The reaction between quadrivalent tin and chromous chloride *proceeds rather slowly,* perhaps because of the presence of colloidal stannic acid. Nevertheless, Brintzinger and Rodis (12) attempted to utilize this reaction for the potentiometric determination of tin. They found it best to titrate at 90–100° C., in the *presence of much hydrochloric acid and potassium or calcium chloride:* 20 cc. of concentrated hydrochloric acid and 30 g. of $CaCl_2.6\ H_2O$ per 100 cc. The oxygen is removed by passing carbon dioxide through the boiling solution for five minutes. Even under these conditions the potential at the end point is established so slowly, that after adding 0.1 cc. of 0.1 *N* chromous chloride solution a *delay of at least three minutes must precede the reading.* Brintzinger and Rodis add 0.1 cc. portions at the break, striving for an accuracy of about 1%, in contrast to the workers already mentioned, who titrated drop by drop at the break to attain an accuracy of several parts per thousand.

A striking improvement in the sharpness of the potential break and in the reliability of the tin value is observed if the solution contains a metal that is deposited after the stannous salt has been formed. This is especially true of *bismuth.*[12] If *quinquivalent antimony* is present, at the change from Sb (V) to Sb (III) a jump (about 0.60 volt) is observed; during the reduction of the stannic salt that follows the titration must be slow enough to prevent the simultaneous production of metallic antimony. Here also, a delay of about three minutes must be allowed after each addition in the vicinity of the break (about 0.05 volt).

With this procedure, Brintzinger and Rodis determined tin successfully, even *in the presence of copper and of iron.*

Because the potential is so slowly established in the reduction of stannic solutions, Schloffer (14) prefers to add an *excess of chromous*

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[12] Compare in this connection the action of bismuth in the titration of iron in chloride solution (16).

sulfate to the solution containing 10% hydrochloric acid and 10–20 g. of potassium or calcium chloride. The excess reducing agent is destroyed with the aid of the *catalytic action* of 2–5 drops of approximately 0.01 *N* *palladous chloride* solution. Under these conditions, the oxidation of the chromous ions by the hydrogen ions (see pp. 132 and 143) is complete within a few minutes in boiling solution. When the potential has risen to $E_H \backsim +0.06$ to 0.11 volt, the flame is removed and the solution is *titrated* with 0.1 *N potassium bromate* or *dichromate solution.* $E_H \backsim +0.42$ volt is taken as the end point potential.

Schloffer uses this procedure also for the titration of *tin in the presence of copper and iron.* He obtains the copper or iron value in the reduction with chromous sulfate, and then the sum of tin and copper (or iron) in the oxidation with bichromate. In the presence of iron, palladium also enters into the titration. It must not be forgotten that the atmospheric oxygen contained in the bichromate solution raises its active strength about 0.3%. A disadvantage of Schloffer's method is that it *cannot be used in the presence of antimony,* because it does not permit the removal of the excess chromous sulfate by palladium.

The *determination of other metals* by reduction with chromous salts is discussed in the references given in the bibliography at the end of this chapter:

Gold: (8, 9, 15); *Iron:* (13, 16, 20); *Bismuth:* (14); *Molybdenum:* (11, 19); *Titanium:* (18).

The *end point potentials* (in the absence of a carrier) for the *separate determinations* with chromous solutions are collected in the Table below. The potentials $E_{Hg_2SO_4}$ are referred to the 2 *N* sulfuric acid-mercurous sulfate electrode.

Reduction Process	Type of solution	E_H	$E_{Hg_2SO_4}$
Hg^{++}/Hg^{+}	H_2SO_4	+0.74	+0.06
$Cr_2O_7^{--}/Cr^{+++}$	"	+0.40	—0.28
Hg^{++}/Hg	"	+0.33	—0.35
Ag^{+}/Ag	"	+0.24	—0.44
Hg^{++}/Hg	HCl	+0.19	—0.49
Cu^{++}/Cu^{+}	"	+0.17	—0.51
Sn^{++++}/Sn^{++}	$HCl+CaCl_2$	+0.06 to +0.11	—0.62 to —0.57
Ag^{+}/Ag	$HCl+NH_4Cl$	+0.07	—0.61
Cu^{++}/Cu	H_2SO_4	+0.06 or +0.14	—0.62
Bi^{+++}/Bi	H_2SO_4+KCl	—0.06	—0.74
Ag^{+}/Ag	$HC_2H_3O_2+NaC_2H_3O_2+NH_4Cl$	—0.10	—0.78

The Determination of Several Metals by a Single Titration. The essential conditions for the determination of two or more metals in the presence of each other have been shown in the foregoing discussions of the single determinations or in the individual potential values. The most important joint determinations that have been investigated are summarized here.

Copper-Mercury. (8, 10). The solution should contain 5% hydrochloric acid and at least 1.5% sodium chloride or the equivalent quantity of another chloride. The titration cannot be carried out in the presence of acetic acid. "Pre-reduction" is used to remove the atmospheric oxygen (see p. 138), since the formation of cuprous ions precedes the precipitation of the mercury.

Copper-Silver. (8, 15, 14). The procedure used for the determination of silver in chloride solution should be employed. Accordingly, the titration is made in the presence of 20–30 g. of ammonium chloride, 5 g. of sodium acetate and "several cc. of acetic acid" per 200 cc. of solution. The reduction of copper to cuprous ion precedes the reduction of the silver. Oxygen is removed by boiling as prescribed on p. 140. Reinäcker recommends this method for the rapid analysis of copper-silver alloys (see in any case p. 145).

According to Schloffer, these metals may be determined in the presence of each other in chloride-free solution. The silver values, however, were often 0.5–1% too high.

Copper-Iron. (14, 16; see also 7). The determination may be made by the method used for copper in *sulfuric acid* solution. Here also the concentration of the sulfuric acid may be between 2 and 15%. "Pre-reduction" may be applied to remove the atmospheric oxygen. It should be remembered that the ferrous ion formed first consumes the atmospheric oxygen more slowly than does cuprous ion, and consequently after adding about 5 cc. of chromous sulfate solution it is necessary to wait several minutes longer before reoxidizing than when copper is determined alone.

If the requirements holding for *chromate* are met, chromate, iron and copper can be determined in the presence of each other.

Schloffer, using the method given, determined *iron* in *copper sulfate* and *iron* and *copper* in *pyrites and chalcopyrites.* The analysis of *arsenopyrites* can be accomplished by oxidizing the trivalent arsenic to the quinquivalent state with a known excess of bichromate and then titrating the bichromate, iron and copper with chromous sulfate.

Copper-Tin (17, 14). The determination in the presence of each other should be made under the conditions set up for the separate determination of tin. The solution should be sufficiently strong with hydrochloric acid and it must also contain much potassium or calcium chloride (see p. 147). Consult Brintzinger and Rodis (17) concerning the analysis of binary, ternary and quarternary tin alloys.

Gold-Copper-Mercury. (8, 15). Since the determination of copper in the presence of gold is possible only if the chloride ion concentration is small, but since, on the other hand, a large chloride ion concentration is necessary for a distinct break between copper and mercury, the conditions at the beginning must be such that only the gold ions are reduced. This will be the case if the solution being titrated contains 2–5% hydrochloric acid. Before proceeding to further reduction bismuth chloride should be added to aid in the transfer of charges and also for each 200 cc. of solution, 15 cc. of freshly boiled concentrated ammonium chloride solution.

Gold-Copper-Silver. (8, 15). In this case, gold and copper are determined first in 2–5% hydrochloric acid. The solution, which should be only slightly over-titrated, is neutralized then with ammonia and treated with the requisite quantities of ammonium chloride, sodium acetate and acetic acid. The oxygen dissolved in these solutions oxidizes the small quantity of silver that has already been formed and also some cuprous ion, so that on further titration there is observed first the break indicating the complete reduction of the copper and then the jump characteristic of the silver.

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PART VI

OXIDATION-REDUCTION INDICATORS

BY

ERNA BRENNECKE

OXIDATION-REDUCTION INDICATORS

General Considerations

One of the most important demands made of a good volumetric method is that it shall offer the possibility of exactly determining the point when the standard solution added is equivalent to the quantity of the material being determined. Therefore, if the reaction itself is not accompanied by a distinct color change it is necessary to use a material that will signal the attainment of the end point, that is an indicator. Acidimetry and alkalimetry which involve colorless solutions almost exclusively are especially dependent on indicators. Consequently, the first intensive studies dealt with indicators suitable to these types of titrations. This matter has been discussed in Part I of this book. In contrast to this situation, the wide applicability of the intensely colored potassium permanganate, and the ease of detecting small amounts of iodine by means of starch obscured for a long time the lack of redox indicators. Attempts to develop new methods employing other standard oxidizing or reducing solutions always encountered the same obstacle: there were no redox indicators that could be generally used [see (119)]. Refuge was taken either in an inconvenient spot test or in an indirect titration involving the iodometric or permanganate back-titration of an excess of the standard reagent or its reduction or oxidation product.

Attempts to supply this need have increased during the past 15–20 years. The efforts have proceeded particularly along two definite lines, which had already led to essential success in acidimetry and alkalimetry:

1. The oxidation potential of the solution was followed during the titration by means of a smooth platinum electrode, that is, the end point was determined *potentiometrically*. The chief value of this "electrometric volumetric analysis" is that it makes possible an intimate study of the oxidation-reduction reactions going on in the solution. So this method becomes the basis for the intensive study of the second indicator method, which is better adapted to practical purposes.

2. The most desired goal in the study of *oxidation-reduction-indicators* is to find a series of dyes that *will immediately show striking and reversible color changes at the attainment of definite oxidation potentials.* These would be analogous to the acid or basic indicators that visibly respond to definite hydrogen ion concentrations. The proper indicator

could be selected then merely on the basis of the known potential of the solution at the end point of the given reaction.

This aim makes it plain why the present discussion of "oxidation-reduction indicators," using the term in the narrower sense, omits some indicators whose value for this type of reaction is acknowledged, but whose indicator action depends on wholly individual properties of the reacting materials. A typical example is starch which, though indispensable in iodometry, is not included here because it is a specific reagent for iodine. For the same reason, there is no discussion here of the various spot tests, such as the use of ferricyanide as external indicator in the titration of ferrous solutions with bichromate.

General Characterization of Oxidation-Reduction Indicators

The characteristic properties of redox indicators will be understood best if those of the *acid-base indicators* are kept in mind. As is well known, the latter are weak to moderately strong acids or bases that exhibit definite color changes when their salts are formed. (The accompanying alteration in constitution of the dye need not enter into this discussion.) They are, therefore, compounds of the same type as those involved in the titration itself and the color change is brought about through a neutralization.

Correspondingly, *a redox indicator ideally* is a material which itself is a *reducing or oxidizing agent.* It indicates the end point of the titration by being oxidized or reduced by a slight excess of the titrant and suffers as a consequence an alteration in constitution, which is made manifest by a striking color change.

A redox indicator then is suited for a particular reaction when *its transition potential,* that is the potential shown by a solution in which the two oxidation stages of the indicator are present in equal molecular quantities, *coincides,* within certain limits, *with the potential of the solution at the equivalence point.*

The numerous intensive studies of Clark, Michaelis and their co-workers[1] show that these purely thermodynamically derived relationships, that were first worked out for inorganic redox systems, can actually be applied to certain organic indicators (122, 91). The study of the connection between potential and dyestuff equilibrium has revealed in a number of cases that these redox systems are reversible.

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[1] In this connection see (120); extensive references to Clark's studies are given in [(121) vol. I, p. 83].

These experiments also showed that the oxidation potentials of the indicators are more or less *dependent on the hydrogen ion activity of the solution* (compare the quinone-hydroquinone electrode). This finding is not surprising if it is noted that most of the redox indicators are multivalent acids or bases, whose degree of dissociation is dependent on the hydrogen ion activity of the solution, and that the oxidation of organic dyestuffs usually involves the loss of two hydrogen atoms. The acid concentration will not affect the two forms of the indicator alike, that is, it will cause a shift of the dyestuff equilibrium.

In addition, the *salt error* caused by the electrostatic forces of the ions present in the solution must be taken into account. Its effect is greater here than in other reactions because, in most cases multivalent ions are involved and furthermore the number of charges on each of the two stages of oxidation is always different [Debye theory of strong electrolytes (123) see also (120)]. Usually the organic compounds involved are only slightly dissociated and consequently the interionic forces affect the system undergoing titration to a greater degree than they do the indicator system.

A fundamental difference between neutralization reactions and reduction-oxidation reactions is the very different significance in the building up of an ion attached, on the one hand to the *loss of hydrogen ions* and to the *loss of electrons* on the other. In redox reactions the change in the structure of the molecule is much deeper seated. Experience shows that as a consequence the *reactions are usually not completely reversible* and that *retardations and side-reactions intervene.* The best attainment of equilibrium, that is, the most complete reversibility of the redox reaction may be expected when the two oxidation stages of a material are formed from each other merely by the gain or loss of one or more electrons. Instances are Fe^{+++}/Fe^{++} and quinone/hydroquinone, i.e. $C_6H_4O_2/C_6H_4O_2^{--}$ (compare in this connection the use of ferrous-o-phenanthroline complex as indicator).

The reduction or oxidation product that is formed initially often suffers an *irreversible secondary change.* An excellent example is the titration of oxalic acid with permanganate. The oxalate ion is first neutralized electrically and then disintegrates into two molecules of carbon dioxide. Correspondingly, when redox indicators are used it must be kept in mind that they may be decomposed during the titration, that is they can not be reconverted completely to their original state. Should this happen, they will consume more of the titrant than is necessary merely to bring about the color change. As a result, the titration generally cannot be carried back and forth repeatedly at will. Such *lack of resistance* of the indicator is especially evident at higher temperatures and if an excess of the oxidizing agent is present during the titration. Dyestuffs that are completely irreversibly changed can be used only in special cases (compare methyl red in the titration of arsenite with bromate, p. 99f).

A further point to be noted when using redox indicators is that it is difficult to measure accurately potentials that are more negative than the hydrogen normal potential or more positive than the oxygen normal potential [for instance Cr(II)/Cr(III)] since they are not fully in equilibrium; otherwise they must liberate hydrogen or oxygen by reaction with the ions of water.

The *sluggishness* exhibited by redox systems is well known from the titration of oxalic acid with permanganate. It is manifested particularly by a variation in the readiness with which these indicators respond to the oxidation-reduction potential of the solution. In certain cases it is necessary, at the end of the titration, to wait for the establishment of equilibrium after the addition of each drop of the reagent. These peculiarities of the redox systems will be discussed individually in the Section dealing with the practical application of these indicators.

Finally, it must be mentioned that *induced reactions* may occur. Sometimes they alone make it possible to use a particular indicator (see for instance, the behavior of diphenylamine in the titration of iron with bichromate). In other cases, the indicator itself may act as intermediary [see for example, (120) p. 151].

From the foregoing it should be evident that *theory* lays the foundation for the use of redox indicators but that, even more than in neutralization reactions, *experimental testing* is essential. From both a theoretical and a practical standpoint, much remains to be done in this field of volumetric analysis. This is all the more true because the studies, by Clark, Michaelis and others, of the potentials of indicators were directed essentially toward the discovery of materials that would be suitable for the *colorimetric determination of the oxidation potentials* obtaining in the metabolism of the living cell. An indicator that can be used for redox volumetric determinations must meet certain other qualifications, especially resistance to irreversible changes. Only a few of the many organic reduction-oxidation systems studied by these workers have been tested as to their applicability to titrations. On the other hand, the most important and most thoroughly studied oxidimetric indicators have not, as yet, been intimately examined regarding their electrochemical behavior.

The most difficult question regarding reduction-oxidation indicators is still the least clarified: the *connection between the change in color and the change in constitution.* There are two opposing viewpoints: one that the color change is due to the production of a quinoid group, the other that the formation of addition (complex) compounds is responsible for the striking colors.[2]

In the following discussion the *most important and most thoroughly tested oxidation-reduction indicators* will be treated in considerable detail. These are:

1. Diphenylamine, diphenylbenzidine, diphenylamine sulfonate;
2. Erioglaucin, eriogreen, setoglaucin, etc.;
3. o-Phenanthroline-ferrous sulfate.

The *essentials of the application of redox indicators are summarized:* The titrant must not be added too rapidly in the neighborhood of the end point, and in general it is not permissible to titrate back and forth repeatedly at will. It is necessary to remember that the oxidizing agent may destroy the indicator during the titration, a fact that is particularly vital when dealing with unproven indicators. In some cases the indicator should not be added until the end point has almost been reached.

SECTION I

Diphenylamine, Diphenylbenzidine, Diphenylamine Sulfonic Acid. In diphenylamine, $C_6H_5NHC_6H_5$, Knop (8, 9) found the first indicator that, to a considerable degree, met the requirements demanded of an indicator suitable for oxidation-reduction titrations.[3] Its serviceability has since been confirmed by many workers (see Bibliography at the end of this Part). It is now the best known and the most thoroughly studied of the redox indicators used for titrations.

GENERAL PROPERTIES OF DIPHENYLAMINE AND ITS DERIVATIVES

Diphenylamine. The intense blue produced by the action of oxidizing agents, particularly nitric acid, on diphenylamine was quite well known from its application in qualitative analysis. The findings of Kehrmann and his coworkers (92, 93)[4] followed by those of Knop (8, 9), Thiel (97), Riehm (98, 99) and Kolthoff and Sarver (38) have led to the following conception of the color change of diphenylamine:

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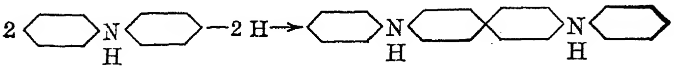
[2] Compare the views of Hantzsch on "carbonium salts."

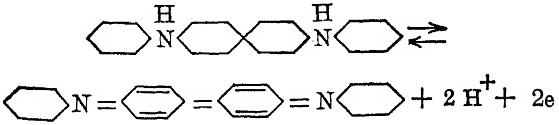
[3] Diphenyl carbohydrazide that was recommended as early as 1906 by Brandt (1, 3, 4, 7) proved too dependent on the conditions surrounding the titration; it is not sufficiently reversible.

[4] See also Wieland (94, 95); likewise Marquerol and Muraour (96).

The very weakly basic colorless diphenylamine when oxidized in acid solution is converted first into colorless *diphenylbenzidine*



which is reversibly further oxidized to the holoquinoid *diphenylbenzidine-violet:*



(compare the equilibrium between hydroquinone and quinone). Under certain circumstances, there is formed as an intermediate product a very slightly soluble green compound, which is usually considered to be a molecular compound of diphenylbenzidine and diphenylbenzidine-violet. According to the newer views, these "meriquinoid salts" produced by oxidation of aromatic amines in acid solution are monomolecular sub-salts in which the uncompensated distribution of the charges may be taken as the reason for the color.[5]

This view as to the cause of the color change of diphenylamine is decidedly not in agreement with the ideas particularly of Madelung, Reiss and Herr (102). Their studies of the deep blue to violet compounds of the para substituted derivatives of diphenylamine and triphenylamine and of the corresponding compounds of the benzidines led them to the conclusion that the color is not produced by a change in the linkage of the atoms in the molecule (resulting from the formation of a quinoid linkage). In their opinion, it is merely a matter of the amine combining with ferric chloride, stannic chloride, chromic acid anhydride, etc. to form pure *addition compounds,* whose structures can be interpreted by the Werner Theory.

Weitz and Schwechten (103, 104), after studying tritolylamine and its compounds with perchloric acid and picric acid, arrived at a similar explanation of the blue compounds formed. However, while Madelung, Reiss and Herr regard the metal atom with the highest valence, the trivalent iron for instance, as the central atom, Weitz and Schwechter postulate the formation of an ammonium-like complex with nitrogen as the central atom.

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[5] See Pfeiffer (124), Weitz (100) and Michaelis (120). Michaelis uses a somewhat different nomenclature: he terms every compound "meriquinoid that is formed by the molecular union of a quinoid-like with a benzenoid-like substance" (that is, all quinhydrones in Pfeiffer's nomenclature) and calls the monomolecular oxidation intermediate products "semiquinones." See also Michaelis (101).

The blue to violet compound produced first from the diphenylamine can be *irreversibly* further oxidized by an excess of the oxidizing agent to yellow or red compounds of unknown composition. This occurs especially at low acid concentration ($pH > 2$). The decomposition is more marked the stronger the oxidizing agent and the higher the temperature.

The *transition potential* of diphenylamine has been determined only in connection with the bichromate-iron titration. Kolthoff and Sarver (38) took the potential at the first appearance or disappearance of the violet that could be detected in the presence of the Cr (III) color; they found this potential to be 0.51 ± 0.01 volt measured against a saturated calomel electrode (i.e. 0.76 ± 0.01 volt against the normal hydrogen electrode). Schollenberger (42), using varying conditions, found 0.52–0.57 volt. The potential, in this case, proved independent of the acid concentration of the solution. The end point potential as measured in the *potentiometric* titrations of the other reactions in which diphenylamine can be used, can not be taken directly as the transition potential of this indicator because, in general, the conditions of the experiments are too different.

Diphenylamine is only *slightly soluble* in water. According to Thiel (97) the solubility is 0.0316 g. per liter at 15° C.; from the figures of Desvergnes [6] it appears to be about 0.04 g. per liter at this same temperature. From measurements of the solubility of diphenylamine in various concentrations of sulfuric acid, Thiel calculated the basic dissociation constant to be 7.6×10^{-14}.

A solution of 1 g. of diphenylamine in 100 cc. of concentrated sulfuric acid, ("1% solution") is generally used for titrations; sometimes a solution one-fifth or one-tenth as strong is used. A solution in syrupy phosphoric acid has been repeatedly recommended. A solution that contains 1.69 g. per liter is 0.01 *M* or (for the transition into diphenylbenzidine-violet) 0.02 *N*.

The indicator solution keeps well; a brown or even a blue discoloration of the solution does not affect its utility.

Lang (41, 51, 58) sometimes does not use the indicator solution directly, but, in a volume of a few cubic centimeters, subjects it beforehand to the reaction occurring in the main titration, so that the indicator is added to the solution to be titrated in the same stage of oxidation in which it will be at the end of the titration. In this way, he largely avoids the indicator correction. [See also Willard and Young (46, 48, 49)].

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[6] See Landolt-Börnstein, Physikalisch-chemische Tabellen. 5th ed., Supplementary Volume for 1931. The statement of Dehn (0.03 g. in 100 cc. of water at 20–25° C.) is admitted by this worker to be not very accurate.

Diphenylbenzidine. On the assumption that it is an intermediate product when diphenylamine is used as redox indicator, attempts were made to use diphenylbenzidine directly, with the expectation that no oxidizing agent would be consumed in its formation and hence the indicator correction would be less.

The slight solubility (see below) of diphenylbenzidine obviously is an obstacle to its usefulness; for instance in the titration of iron with bichromate it reacts much more slowly than diphenylamine. As to the color change, it has the same value as the latter indicator in the titration of oxidizing agents. In these cases the presumption that diphenylbenzidine *requires a smaller indicator correction* has been confirmed repeatedly (compare, for instance, Table II, p. 170 and the titration of vanadic acid with ferrous sulfate, p. 173).

Kolthoff and Sarver (38) found that diphenylbenzidine has the same *transition potential* as diphenylamine in the bichromate-ferrous titration, namely 0.51 ± 0.01 volt measured against a saturated calomel electrode. They took this as confirmation that diphenylbenzidine is actually produced from diphenylamine in the titration.

These workers found the solubility of diphenylbenzidine in water to be 0.06 ± 0.005 mg. at 25–50° C. In 2 N hydrochloric acid it is about five times as great, in sulfuric acid of the same normality the increase in solubility is less. The ionization constant is 2×10^{-14}.

The *solutions most commonly used* for indicator purposes contain 1 or 0.1 g. of diphenylbenzidine in 100 cc. of concentrated sulfuric acid (1% or 0.1%) or 0.1 g. of the indicator in 10 cc. of concentrated sulfuric acid diluted with 90 cc. of glacial acetic acid. A solution containing 3.38 g. of diphenylbenzidine per liter would be 0.01 M; for the change into diphenylbenzidine-violet this would be 0.02 N. [Compare also (56)].

Solutions of diphenylbenzidine also become discolored on standing, even when they have been made from a pure preparation (98, 99).

Diphenylamine-p-Sulfonic Acid. Kolthoff and Sarver (43) tried to improve the indicator properties of diphenylamine by introducing a strongly polar group into the molecule. They prepared *diphenylamine-p-sulfonic acid,* $C_6H_5NHC_6H_4SO_3H$, and their studies led them to believe that it has the same oxidation mechanism as diphenylamine.

The *chief advantages* of diphenylamine sulfonic acid are its solubility in water, its strikingly sharp color change and the fact that it can be used in the presence of tungstic acid. (For details see the discussion of the bichromate-ferrous titration).

The color change in the bichromate-ferrous titration from green through grey to red violet occurs at a somewhat higher *potential* than those of its two related indicators, namely at 0.59–0.60 volt, referred to the saturated calomel electrode.

A *water solution* of barium diphenylamine sulfonate can be used directly in titrations. Kolthoff and Sarver sometimes used 0.005 *M* solution (corresponding to 3.17 g. of the barium salt per liter) and sometimes 0.2% solution. If the barium ion interferes, the sulfonate can be treated in advance with sodium sulfate.[7]

(d) Among numerous *substitution products of diphenylamine* that Hammett, Walden and Edmonds (53, 54) studied with respect to their usefulness they found p-nitrodiphenylamine and 2,4-diaminodiphenylamine to be excellent indicators for certain titrations. It is of special interest that these substitutions result in compounds whose transition potentials diverge in definite directions from that of diphenylamine. In the first case, the potential, under comparable conditions, is about 0.3 volt higher, in the second, about 0.06 volt lower. According to Syrokomsky and Stiepin (58b) o-diphenylamine carboxylic acid is also a very good indicator. Its molar oxidation potential is 1.08 volt. Kirssanow and Tscherkassow (58d) found that N-phenylanthranilic acid is an excellent redox indicator.

Sarver and Fischer (57) found that the indicator properties of sodium diphenylbenzidine polysulfonate resemble, to a great extent, those of diphenylamine sulfonate.

USE OF DIPHENYLAMINE AND ITS DERIVATIVES IN OXIDIMETRIC VOLUMETRIC ANALYSIS

The Titration of Ferrous Salt with Potassium Bichromate and Vice Versa

Indicator: Diphenylamine

The most frequent and also the most important application of diphenylamine is in the titration of ferrous solutions with bichromate. Since its use obviates the tedious spot tests, this indicator now makes possible the easy utilization of the advantages of bichromate over permanganate, namely, stable, exact solutions easily prepared.

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[7] See Furman, Part II of this Book, p. 33; also Willard and Young (48).

Procedure. The titration is best carried out by the procedure given by Knop (8, 9). The solution containing 0.1–0.15 g. of iron is acidified with 20–25 cc. of sulfuric acid (1 : 4, about 7 N) or 20 cc. of hydrochloric acid (1 : 1, about 6 N) and diluted to 150–250 cc. Then 15 cc. of phosphoric acid mixture (150 cc. of conc. H_2SO_4, (sp. gr. 1.84) + 150 cc. of H_3PO_4, (sp. gr. 1.7) diluted with water to 1 liter) to bind the ferric ions into complexes and 3 drops of 1% indicator solution are added and the titration is made with 0.1 N bichromate solution.

Knop (9) gives the following criteria for the end point of the titration: "Near the end point, the green color of the solution deepens to blue green or—in the presence of considerable quantities of iron—even to blue grey. From this point on the bichromate is added dropwise. The point at which 1 drop produces an intense violet blue, which is unchanged by further addition of bichromate, is taken as the end point. A titration in which 20–30 cc. of 0.1 N bichromate solution is consumed gives the sharpest end point." Knop observed that with about twice this quantity of iron, the blue grey shade that precedes the real change is somewhat stronger. However, even then, particularly after a little practice, the end point can be hit exactly. The error is at most one drop: 0.03 cc.

Knop subtracts 0.05 cc. as *indicator correction* from the volume of bichromate used (see however, p. 167).

When dealing with quantities of iron quite different from those just given, it is best to alter correspondingly the quantities of the added materials. With titrations involving about 0.2 g. of iron, under the above conditions, the exact recognition of the end point can be made somewhat easier by the use of a *reference solution.* This is prepared by dissolving 2 g. of chrome alum in the cold in 260 cc. of water. (This solution slowly turns greenish and therefore can be used only for 2–3 days.) The reference shade differs by about 0.014 cc. of 0.1 N bichromate from the deep blue violet that stays unaltered on further addition of the oxidizing agent. Of course, the same shade is not always hit; in this case the titration should be carried to a shade distinctly bluer than the standard (see p. 167).

If weight burettes are used, it is possible, after some practice and with good illumination (*the titration is impossible in artificial light*) to secure agreement within 0.06%. It must be remembered however, that the *color change is not always the same* when ferrous solutions are titrated with bichromate, a point to which Sarver (26) especially has called attention [see also (105)]. The distinct blue violet is sometimes slow in appearing. In this case a back-titration can be made with a known ferrous solution and the color change once again produced with bichromate.

Under the conditions of the titration, diphenylamine in *sulfuric acid solution* is so negligibly decomposed by bichromate that it makes no difference whether the indicator is added at the beginning or toward the end of the titration. The effect is quite different in *hydrochloric acid solution*; if the indicator is added at the beginning of the titration there is an over-consumption of bichromate of about 0.06% (=0.02 cc. of 0.1 N $K_2Cr_2O_7$) compared with the result if the introduction of the indicator is delayed until near the close of the titration.

The *acid content of the solution* should not greatly exceed that prescribed above. Although Knop obtained practically the same results with 6 cc. and 40 cc. of 1 : 1 HCl in 200 cc. of solution, at still higher acid concentrations the color change appeared about 0.2% too soon. The writer has confirmed Schollenberger's statement (42) regarding the effect of a higher sulfuric acid concentration: in the presence of 40–50 cc. of approximately 7 N sulfuric acid in a titration volume of about 200 cc. (containing 0.20 g. of iron) the color change and consequently the result is uncertain; the iron values are also too low by several parts per thousand. According to Someya (15) *acetic acid* acts in a peculiar way. The color change is sharp, to be sure, but the volume of bichromate must be corrected by adding 0.32 cc.

Since the indicator is excellently reversible, *bichromate*, in the presence of sulfuric acid, *may be titrated with a ferrous solution* with like accuracy, even though the indicator is added to the bichromate solution at the beginning of the titration. An agreement of 0.1% is easily obtained. The color change is altered somewhat but readily detected.[8]

The observation that *ammonium fluoride can be used in place of phosphoric acid to bind the ferric ions into complexes* is of importance in the determination of bivalent iron in minerals (compare 26, 39, 42). In the presence of fluoride, the color change is even sharper, although its appearance is slowed up considerably. In this case, the most suitable end point is the disappearance of the green and the appearance of a medium blue. The deep violet appears only if an excess of bichromate is titrated back with ferrous solution (see p. 166). The operator should wait several seconds after each addition of bichromate; at the end point the new color persists for more than a minute.

When working with solutions containing ammonium fluoride, particular note must be made of the well known *sensitivity of ferrous solu-*

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[8] See Furman (13) concerning the determination of chromium in steel.

tions to oxidation by the air. Unless special precautions are taken, errors of about 1% are easily possible. The results are better (error = –0.2–0.5%) if the solution is acidified with 40–60 cc. of sulfuric acid, 1:4 (compare 39, 106). The findings are the same as when phosphoric acid is used, provided the water and sulfuric acid are placed in the titration flask and freed of air by gradually adding 1–2 g. of potassium bicarbonate before introducing the ferrous solution [see (39)]. It is best to add the ammonium fluoride just before starting the titration. For 0.20 g. of iron, 1.2 g. of ammonium fluoride is sufficient; but accurate results (within 0.1%) are obtained when as much as 5 grams of ammonium fluoride is present.

The Behavior of the Indicator. Knop showed that *bichromate alone produces no color change in an acidified solution of diphenylamine.* Under the conditions obtaining in the titration, *ferric ions* produce a slight violet color rather rapidly, if no phosphoric acid is present. If, however, the Fe(II)/Fe(III) potential is lowered by the addition of phosphoric acid or ammonium fluoride, the ferric solution to which diphenylamine has been added will become absolutely colorless within five minutes. The ferric ions, even at this low concentration, are still significant in the production of the color change with bichromate; a fact that is quite evident from the statements of Knop (8,9) and Benedetti-Pichler (27) and from the writer's own studies. Obviously the rather slow appearance of the color change when fluoride is present is connected with this. Using the observations of Kehrmann and Micewicz (92), Knop assumes that the ferric ion produces from the diphenylamine first diphenylbenzidine, which then is converted into diphenylbenzidine-violet by chromic acid.

The *reaction between ferrous ions and bichromate* has special significance in the production of a sharp color change. Its influence may be observed easily particularly in the presence of fluoride, because a solution that has been over-titrated with bichromate turns a deeper violet on the addition of the first drop of ferrous solution (compare p. 190 and p. 192).[9]

In the light of these facts it can be seen why the *indicator correction* cannot be determined accurately here by the method which yields such excellent results in acidimetry, for instance; that is, by treating a solution like that at the equivalence point with bichromate until the color change is produced. The results are still more uncertain if small quantities of bichromate are titrated back with ferrous solution.

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[9] The oxidation of the indicator can also be brought about by the reaction of bichromate and arsenious solution (51). For the interpretation of these analogous observations compare the statements of Wagner and Priess (107) and Wagner (108) on the formation of quinquivalent chromium. See also Zintl and Zaimis (109), and Lang (35, 51, 55) regarding chromium (IV) salts as intermediate stages.

Knop obviously determined the indicator correction of 0.05 cc. (see p. 164) by comparing the titration data with those obtained with permanganate. In contrast, the writer, using weight burettes and a solution prepared from bichromate that had been repeatedly recrystallized, obtained excellent agreement between the parallel trials and found that the bichromate titration of bivalent iron, without correction, gives practically the same (or rather somewhat lower) results as the permanganate titration.[10]

The permanganate solution, in this case, was standardized against sodium oxalate (Sörensen) and the iron-permanganate titrations made with the aid of *erioglaucin* and *setoglaucin* as indicators. In this titration the indicator correction can be determined very well directly (see p. 185). The deviation of the reference color (see p. 164) to which the iron-bichromate titration was usually carried, was about 0.014 cc. of 0.1 *N* bichromate from the change point given by Knop.

The *dependence of the color change on the accompanying conditions* is evidenced by the fact that this *change is not always the same.* In some instances the reference shade could not be reached at all. When this happened the titration was carried to a shade somewhat bluer than the standard [compare the similar observations of Lang (55)].

For purposes of comparison, the *indicator corrections found with 0.01 N solutions* will be given:

Furman (13) determined the indicator correction for the titration of 0.01 *N* bichromate solution with 0.02 *N* ferrous sulfate by comparison with the potentiometric titration and found a correction of 0.07 cc. of 0.02 *N* ferrous sulfate for 0.2 cc. of 0.1% indicator solution. Recalculated to the conditions of Knop's titration, this correction becomes 0.05 cc. of *0.1 N* bichromate.

Kolthoff and Sarver (43) determined the indicator correction of diphenylamine for titrations with 0.01 *N* and 0.001 *N* solutions of ferrous sulfate and potassium bichromate and, at the same time, *the dependence of the correction on the indicator concentration.* They, too, standardized the ferrous solution potentiometrically. Their study showed that a larger volume of oxidizing (or reducing) solution is required to bring about a distinct change when a larger quantity of indicator is present. With up to 0.3 cc. of 0.17% of diphenylamine solution and in a total volume of 45 cc., the correction approximately corresponds to the quantity theoretically required to form diphenylbenzidine. (See Tables I and II, p. 170.)

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[10] In this connection compare Eppley and Vosburgh (110) concerning the potentiometric iron-bichromate titration. In view of this work, there obviously is an error in Kolthoff and Furman "Potentiometric Titrations," p. 276, New York, 1931; see also Willard and Gibson (40a). Riehm (98) observed the beginning of the color change before the oxidation of the diphenylamine to diphenylbenzidine was complete.

The Use of Diphenylamine in the Titration of Iron with Bichromate in Special Cases. If the *iron is present in the trivalent condition* and if, as is usually the case, it is *reduced with stannous chloride* in strong hydrochloric acid solution, the effect of stannic chloride and mercuric chloride on the indicator must be taken into account. According to Kolthoff [38, 43 and 121, vol. 2, p. 285] mercuric chloride somewhat retards the change of diphenylamine [see also (35)]. Nevertheless, according to Knop, the titration with bichromate is more exact than the Zimmermann-Reinhardt method with permanganate; above all, it is less dependent on the quantity of iron involved. The color change is somewhat modified.

Benedetti-Pichler (27) tested the applicability of the Knop indicator method to the *micro-determination* of bi- and trivalent iron. He found in the titration of about 0.5 mg. of iron with 0.004 *N* bichromate solution, that the greatest deviation from the average value was less than 0.5%. If the iron was present in the trivalent state, it was reduced with stannous chloride. He obtained with 0.2–0.54 mg. of iron a maximum deviation of 3% from the known content.

Among the foreign materials that may be present at the iron titration, *tungstic acid* has a surprisingly disturbing effect. Even traces of this material completely inhibit the indicator action, because any blue that has been formed cannot be discharged again. Consequently all the tungsten must be removed beforehand.[11]

Copper salts and arsenious acid interfere in the titration of iron with bichromate, independent of the indicator (8, 9, 14). While quantities of copper of less than one milligram have no effect, larger amounts accelerate the oxidation of the ferrous salt by the air. Trivalent arsenic, on the other hand, is partially oxidized along with the iron, and increasingly so, the more iron there is present [compare (71)]. See (8) regarding the titration in the presence of quinquivalent antimony.

Knop found that more than 0.1 mg. of *platinum* leads to distinctly high iron values.

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[11] See (42) and (121) vol. 2, p. 285; also Furman, p. 172 and Willard and Young, p. 174.

The titration of iron with bichromate in the presence of diphenylamine is particularly to be recommended because of the distinct color change when considerable quantities of ferric iron, trivalent *chromium, nickel* and *cobalt* salts are present. Zinc and manganese have no effect. According to (14) it is not necessary to remove colloidal silicic acid. Organic compounds, in general, do not interfere, in marked contrast to their behavior in permanganate titrations.

Indicator: Diphenylbenzidine

As mentioned before, diphenylbenzidine changes too slowly to permit its being used in the titration of iron with bichromate. However, it is just as good as diphenylamine in the reverse titration. According to Willard and Young (29) both indicators give the same results in this case. The writer also has found, that in the presence of diphenylbenzidine (especially with 3 drops of 1% solution) only about 0.05–0.1% of 0.1 *N* ferrous solution more was consumed than when diphenylamine was used as indicator. In these comparative titrations, the procedure prescribed by Knop was strictly adhered to and the titrations, with weight burettes, were carried to a standard shade (see p. 164).

Kolthoff and Sarver determined the *dependence of the correction on the indicator concentration* for diphenylbenzidine just as they did for diphenylamine. The figures are given in Table II, p. 170.

Willard and Young used diphenylbenzidine especially in the *determination of chromium in steel* (see p. 173).

Indicator: Diphenylamine Sulfonic Acid

Barium diphenylamine sulfonate is distinctly different from diphenylamine and diphenylbenzidine in that it gives a *sharp color change* to red violet (see p. 163). Using the Knop conditions, as little as 0.005 g. of 0.1 *N* bichromate can be dealt with at the end point of the titration without a reference solution. To be sure, *larger indicator corrections* are necessary. For example, in titrating iron in the presence of 0.75 cc. of 0.19% of barium sulfonate solution, 0.052 g. of 0.1 *N* bichromate solution had to be subtracted from the volume used, while the subtraction for 0.40 cc. was 0.024 g., which for 0.20 g. of iron amounts to 0.15% or 0.07%. This signifies that one mole of sulfonate consumes two equivalents of the oxidizing agent. Recalculation of the values in Table I to the conditions used here would increase the corrections by about 0.1%. These findings are the results of the writer's own experiments.

Kolthoff and Sarver determined with this indicator also the *dependence of the corrections on the quantity of indicator* for titrations with 0.01 *N* and 0.001 *N* bichromate and ferrous sulfate solutions. For the sake of easy comparison, the values found by Kolthoff and Sarver for all three indicators are given in Tables I and II. The solutions of diphenylamine and of diphenylbenzidine were 0.17% (0.01 and 0.005 *M*, respectively) while the solution of barium sulfonate was 0.32% (0.005 *M*).

TABLE I

Indicator Corrections for the Titration of Iron With Bichromate

10 cc. of 0.01 or 0.001 *N* $FeSO_4$ + 10 cc. of 25% H_3PO_4 + 1.2 cc. of conc. H_2SO_4 + 15 cc. of H_2O, titrated with 0.01 or 0.001 *N* Bichromate

Indicator Solution	Diphenylamine Excess of Bichromate		Diphenylamine sulfonate Excess of Bichromate	
	0.01 *N*	0.001 *N*	0.01 *N*	0.001 *N*
cc.	cc.	cc.	cc.	cc.
0.02	0.01	0.21	0.02	0.21
0.04	0.04	0.41	0.05	0.44
0.10	0.10	0.95	0.18	0.93
0.20	0.21	1.90	0.34	1.85
0.30	0.39	....	0.51	3.48
0.50	0.63	....	0.75–0.90	....

TABLE II

Indicator Corrections for the Titration of Bichromate With Ferrous Solution

10 cc. of 0.01 *N* Bichromate + 10 cc. of 25% H_3PO_4 + 1.2 cc. conc. H_2SO_4 + 15 cc. H_2O, titrated with 0.01 *N* Ferrous Sulfate

Indicator Solution	Too little ferrous solution consumed		
	Diphenylamine	Diphenyl benzidine	Diphenylamine sulfonic acid
cc.	cc.	cc.	cc.
0.02	0.04	0.02	0.05
0.04	....	0.04	0.13
0.10	0.24	0.10	0.31
0.20	....	0.17	0.58
0.30	0.63	0.24	0.95
0.50	....	0.36	....

Barium diphenylamine sulfonate is obviously *less resistant* to oxidizing agents than diphenylamine and diphenylbenzidine, because the quantities of bichromate consumed increase usually by several hundredths of one per cent when the end point is called forth several times. On the other hand, the corrections decrease by several hundredths of one per cent if the indicator is not added until near the end of the titration. The strikingly greater correction when *bichromate is titrated with ferrous sulfate* can be seen in Table II.

The writer has found that when about 35 cc. of 0.1 *N* bichromate solution is titrated in the presence of 0.75 cc. of 0.1% indicator solution, the change occurs about 0.3% too soon if the indicator is added at the start and the titration finished immediately.[12] Therefore, while a bichromate solution containing diphenylbenzidine may be allowed to stand about 15 minutes, a like exposure of diphenylamine sulfonate will lead to considerable error (43). When the titration was finished without delay, the correction, under the same experimental conditions, was quite constant, even though the end point was reached twice by titrating back and forth.

The sharpness of its end point makes diphenylamine sulfonate particularly suitable for titrations in which the detection of the change is made difficult by special circumstances, such as the presence of *highly colored materials,* in *micro-titrations* and when the *illumination is poor.*

The fact that *tungsten* does not affect the color change of this indicator is important in *steel analysis* (see however p. 168).

Finally, mention must be made of the observation of Kolthoff and Sarver that the acid concentration of the solution to be titrated may be varied within wider limits when sulfonate is used than is permissible with diphenylamine or diphenylbenzidine.

The Titration of Vanadic Acid with Ferrous Sulfate Solution

In addition to their use in iron-bichromate titrations, diphenylamine and diphenylbenzidine have been applied particularly in the determination of vanadic acid or vanadate with ferrous sulfate. This titration is important in *steel analysis.* The end point was determined potentiometrically until Furman (13) described the first practical method of using *diphenylamine* for this purpose. Stimulated by the work of Cone and Cady (see p. 176), Willard and Young (30,31) and later Kolthoff and Sandell (37) used *diphenylbenzidine* because of its *smaller indicator correction.* The main objective of these studies was to develop a serviceable method for the determination of vanadium in various types of steel, which would permit at the same time, so far as possible, the determination of the chromium that is usually present. Compare also (40).

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[12] The back-titration was always carried to the first appearance of red violet, that is, to the same end point that was taken in the titration of ferrous solution with bichromate.

The indicators, at the end point, turn to a pale shade, usually greenish. This can be seen easily over the blue color of the vanadyl ion, even with 0.2 g. of vanadium. If chromium and iron are present a grey to blue green color appears. Sufficient *phosphoric acid* must always be present because of the effect of the trivalent iron on the indicator.

Diphenylamine. Furman, as well as Willard and Young, showed that when vanadium is titrated in hydrochloric or sulfuric acid solutions of various concentrations, the change of diphenylamine is sluggish, even though the results are independent of the acid concentration. *The change is sharper if enough acetic acid or sodium acetate is present.*[13] Since the selective reduction by sodium perborate (111) of chromic acid in the presence of vanadic acid (following oxidation with permanganate) requires similar conditions, Furman titrated the vanadium in acetic acid solution. On the other hand, when determining the sum of vanadic and chromic acids, after oxidizing with ammonium persulfate (with addition of silver nitrate), he used mineral acids in the solutions.

The results were satisfactory for vanadium and chromium, even when quinquivalent *arsenic* and sexivalent *uranium* were present. *Tungsten* had to be removed completely beforehand (see p. 168).

Furman determined the *necessary indicator corrections* by simply titrating a known quantity of vanadium in the presence of varied amounts *of diphenylamine.* He found a *clear proportionality between the correction and the quantity of indicator:* for each 0.2 cc. of 0.1% diphenylamine solution, the volume of 0.02 *N* ferrous sulfate should be increased by 0.06 cc. This correction is not changed appreciably if the acid concentration is raised from 5 cc. to 20 cc. of concentrated hydrochloric or sulfuric acid per 125 cc. The correction amounted to more than double, that is, to 0.15 cc. of 0.02 *N* ferrous solution per 0.2 cc. of 0.1% diphenylamine solution when, following the directions of Willard and Fenwick, the titration was made in the presence of 25 volume per cent glacial acetic acid and 10–20 g. of *crystallized sodium acetate* per 100–200 cc. of solution. He recommends the use of as much indicator as will give a correction of 0.05–0.15 cc. of the titrant. He also advises adding 2–5 volume per cent of phosphoric acid (sp. gr. 1.7).

Diphenylbenzidine. Willard and Young made an intensive study of the utility of *diphenylbenzidine* for the titration of vanadic acid with ferrous sulfate under the conditions obtaining in the *analysis of steels.*

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[13] Compare (70, 72) concerning the dependence of the vanadium potentials on the acid concentration.

To reach a sharp end point, they recommend that all excess sulfuric and hydrochloric acid be always treated beforehand with somewhat more than the equivalent quantity of sodium acetate, and even when vanadium and chromium are to be determined together. They also specify the addition of 25cc. of phosphoric acid (sp. gr. 1.37 = concentrated acid diluted with an equal volume of water) per 300 cc. for 4 g. of iron. The titration was not begun until after 5 minutes, so that the blue indicator color had ample time to develop completely. This delay should be adhered to closely, otherwise different corrections must be applied (see Kolthoff and Sarver, p. 176).

Willard and Young *prepare the solution* for the titration of the vanadium by *selectively oxidizing* the vanadium in the solution containing trivalent chromium by means of *potassium bromate,* sufficient hydrochloric acid and ammonium sulfate being present. The latter serves also to eliminate the excess bromate. Any chromic acid that may have been formed is reduced with hydrogen peroxide. When determining the sum of vanadium and chromium, these workers, like Furman, oxidize with ammonium persulfate.

To simulate as closely as possible the conditions met in practice, Willard and Young, with the aid of a synthetic steel solution, determined the *corrections for various volumes of 0.1% indicator solution.* In the presence of 4 g. of iron, 100 mg. of chromium and 12 mg. of vanadium, under the conditions just outlined, they found the values given in Table III, column 4. These figures represent the under-consumption of 0.025 *N* ferrous sulfate solution due to the oxidation of the indicator. (The ammonium vanadate consumed 10.77 cc. of 0.025 *N* ferrous sulfate in the potentiometric titration).

TABLE III

1	2	3	4
Indicato	0.1% indicator solution cc.	Total consumption of 0.025 *N* ferrous sulfate cc.	Indicator solution in cc. of 0.025 *N* ferrous sulfate
Diphenylamine	1.5	10.09	0.68
	1.0	10.26*	0.41*
Diphenyl-benzidine	1.5	10.32	0.45
	1.0	10.46	0.31
	0.8	10.55	0.22
	0.6	10.60	0.17
	0.4	10.64	0.12

* This obviously is a printer's error; it must be either 10.36 cc. and 0.41 cc., or 10.26 cc. and 0.51 cc.

Here again there is a clear proportionality between the *correction and the quantity of indicator:* each 0.1 cc. of *diphenylbenzidine* solution consumes 0.03 cc. of 0.025 *N* ferrous sulfate solution. The *difference* between the corrections for *diphenylamine* and *diphenylbenzidine* is quite striking.[14]

The effect of the indicator on the consumption of the titrating solution proved independent of the iron content, of the volume of the solution and of the quantity of acid present, in so far as all mineral acids, except phosphoric, were buffered by the addition of sufficient sodium acetate. The temperature should not be above 40° C. (13, 12). Willard and Young generally used 0.6–0.8 cc. of diphenylbenzidine solution, and applied a correction of 0.18–0.24 cc. of 0.025 *N* ferrous sulfate solution.

This procedure can be used with *tungsten-chromium-vanadium steels* only if the *tungsten* is precipitated previously (as WO_3). If the operator wishes to avoid this separation, the potentiometric titration may be made satisfactorily in the presence of the tungsten. Both methods give excellent and concordant results, even in the presence of a little molybdenum. After precipitating the tungstic acid, sometimes a 5 minute delay after the addition of the indicator is not long enough; at times the color does not appear until 30 minutes have elapsed. A satisfactory titration could still be made, however. The elimination of the disturbing influence of the tungsten by adding fluoride is discussed in (41) and (58).

Kolthoff and Sandell (37) determined vanadium essentially in accordance with the directions of Willard and Young and confirmed them in every particular. With 0.03–0.002 g. of vanadium together with 1.5 g. of iron and 0.02–0.04 g. of chromium, they obtained deviations of from 0.1 to 0.2 mg. of vanadium, corresponding to 0.1 to 0.2 cc. of 0.025 *N* ferrous sulfate solution.

Diphenylamine Sulfonic Acid. Willard and Young (46, 48, 49) tested *diphenylamine sulfonate,* which is insensitive to tungsten, in the determination of chromium and vanadium. They *oxidized the indicator before the titration* (see p. 161) to diminish the rather large indicator error that was encountered (see p. 169f).

Comparison of the Various Indicator Corrections. In connection with the *indicator correction* in the vanadium-ferrous sulfate titration, Kolthoff and Sarver made several experiments supplementary to those on the iron-bichromate titration (p. 169):

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[14] The correction in the presence of sodium acetate found by Furman would give 0.06 cc. of 0.025 *N* ferrous sulfate for 0.1 cc. of *diphenylamine* solution.

They titrated 10 cc. of 0.01 *N* *vanadate* solution in the presence of 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc. of water, and varying volumes of indicator solution with 0.01 *N* ferrous sulfate solution. With *diphenylamine, diphenylbenzidine* and *diphenylamine sulfonate* they obtained practically the same corrections as in the corresponding trials with *bichromate* (compare Table II, p. 170). Vanadate and bichromate differ only in the speed of the action on the indicator in the absence of ferrous iron. As the speed is greater with vanadate than with bichromate, Kolthoff and Sarver suggest that the titration be begun as soon as the indicator is added.

TABLE IV

INDICATOR CORRECTIONS FOR THE TITRATION OF VANADATE WITH FERROUS SOLUTION

Indicator Solution* cc.	Deficit in Consumption of 0.01 *N* Ferrous Sulfate, cc.		
	Diphenylamine	Diphenylbenzidine	Diphenylamine sulfonate
0.02	0.03	0.03	0.03
0.04	....	0.05	0.12
0.10	0.20	0.11	0.30
0.20	0.40	0.20	0.60
0.30	0.63	0.29	0.95

* 0.01 molar diphenylamine; 0.005 molar diphenylbenzidine and diphenylamine sulfonate.

If the corrections given in Table IV are compared with those found by Willard and Young (or Furman) *for the same quantity of indicator* (taking into account the different concentrations of the indicator solutions and of the ferrous sulfate solution) the result is:

TABLE V

Quantity of Indicator	Corrections in cc. of 0.025 *N* Ferrous Sulfate Solution		Observer
	Diphenylamine	Diphenylbenzidine	
0.89 cc. of 0.17% =1.5 cc. of 0.1% solution	0.76	0.36	Kolthoff and Sarver
	0.68	0.45	Willard and Young
	(0.36)	....	Furman (calculated)
	(0.90)	....	
0.59 cc. of 0.17% =1.0 cc. of 0.1% solution	~0.50	0.24	Kolthoff and Sarver
	0.41(?)	0.31	Willard and Young
	(0.24)	....	Furman (calculated)
	(0.60)	....	

Table VI presents—according to Kolthoff and Sarver—the errors that arise with the use of 0.2 cc. of 0.005 *M* sulfonate solution (under the above conditions) if there is some delay after the addition of the indicator.

TABLE VI

Period of Delay....	0	5	10	15	30 minutes
Correction.........	0.58	0.62	0.68	0.74	0.76 cc. of 0.01 *N* $FeSO_4$

The Titration of Zinc with Potassium Ferrocyanide

The behavior of *diphenylamine* and *diphenylbenzidine* in the titration of zinc with ferrocyanide, at first glance, does not seem comparable with their indicator action in the titrations already discussed. However, as far as they are concerned this is an oxidation-reduction reaction:

Ferricyanide is usually present in potassium ferrocyanide solutions that have stood for some time, or if necessary, a small quantity can be added. In the presence of zinc-ferrocyanide, the ferricyanide produces a blue or blue violet coloration of the indicator, and at the first drop of excess ferrocyanide solution this color changes to a pale yellow green.[15]

Procedure: As in the other procedures for the ferrocyanide method of determining zinc,[16] it is essential to work, *so far as possible, under uniform conditions,* if concordant results are to be obtained. Above all, the titration must not be carried out too rapidly and the solution must be shaken well throughout the titration, since otherwise it is quite easy to over-titrate.

Cone and Cady (22), who first proposed the use of diphenylamine and diphenylbenzidine in the *titration of zinc with ferrocyanide,* dissolved 0.2 g. of zinc oxide in 15 cc. of 30% sulfuric acid, diluted the solution with 100 cc. of water, and after adding 10 g. of ammonium chloride and several drops of 1% indicator solution titrated at room temperature with approximately 0.05 *M* ferrocyanide solution containing 0.3 g. of potassium ferricyanide, approximately 0.001 mole per liter. If the titration is slow enough, the color change is quite sharp and permanent; the writer has confirmed these points in her own studies. As the ferrocyanide is added, the solution at first turns a deeper blue, then becomes paler and finally takes on a distinct violet shade, which goes over into a yellow green at the end point of the reaction. If the titration is made somewhat faster, the transition from the blue into violet escapes notice and the end point is easily passed. Should this happen, some zinc solution of known strength is run in and the titration continued; the sharp change from violet to yellow green will then appear without fail. As early as 1922 Urbasch (114) called attention to the fact that in the zinc-ferrocyanide titration it makes a difference if, before the final titration, the end point has previously been over-run to a greater or lesser degree. If the over-titration was considerable, the excess consumption was several parts per thousand. Kolthoff's (25) results reveal this same effect and the writer, who carried out her experiments according to the instructions of Cone and Cady, corroborates these findings. The values agree within 1–2 parts per thousand, when the titrations were made under *uniform conditions*. The deviation from the known quantity of zinc ranged from —1.1 to —1.3%, as compared with the potentiometric titration.

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[15] Compare Hope, Ross and Skelly (58a) concerning the quite similar behavior of diphenylbenzidine in the titration of indium with potassium ferrocyanide in a solution containing 60 volume per cent of glacial acetic acid.

[16] See Brennecke (112) concerning the potentiometric determination; the literature on the earlier studies will be found there. See also Laur (113).

Kolthoff modified the directions of Cone and Cady. The chief change was that he titrates at 60° C., in order to hasten somewhat the attainment of equilibrium at the first appearance of the color change. He also made a special study of the effect, on the final result, of adding larger amounts of acids and ammonium salts, and made the peculiar discovery that the presence of *ammonium salts* is *indispensable* to the color change, if the titration is made at 55–60° C. On the other hand, *aluminum salts* inhibit the change.[17] Compare also (45).

Diphenylbenzidine does not differ from *diphenylamine* in the end reaction. Cone and Cady, however, observed that every drop of the latter indicator beyond 2 or 3 drops caused a decrease of about 0.03 cc. in the ferrocyanide consumption, while with diphenylbenzidine the results are quite independent of the volume of indicator solution. In contrast, the writer has found that an *increased consumption* of about 0.06 cc. of ferrocyanide followed when 6 instead of 2 drops of diphenylamine solution were used. With 10 drops of the same indicator solution a transition could no longer be detected.

Kolthoff (34) studied the reverse titration of *ferrocyanide with zinc* solution. A delay in the first appearance of the color change was observed here also. The quantity of potassium ferricyanide added at the beginning had no effect on the final result. This is also true for the quantity of *diphenylamine,* provided 1–20 drops of 1% solution are used. However with 20 drops the color change is not permanent; probably the blue compound reacts with unchanged diphenylamine to form the intermediate oxidation product (meriquinoid formation, see p. 160). In this connection see also (98, 99).

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[17] See (115) and (116) regarding the disturbing effect of aluminum salts in the potentiometric titration of zinc with ferrocyanide.

With 1–10 drops of 1% *diphenylbenzidine* solution the same end point was obtained as with diphenylamine, but the transition was not so distinct (compare p. 162).

Behavior of the Indicator. In the zinc-ferrocyanide titration, *diphenylamine* shows a *characteristic behavior* similar to that exhibited in the iron-bichromate titration: If a quantity of potassium sulfate equivalent to that produced in the reaction between ferrocyanide and zinc is dissolved along with the same quantity of sulfuric acid and indicator in the volume of water corresponding to the final volume of the titration, then not the slightest blue is produced by the addition of 1 cc. of 1% ferricyanide solution. Nor does the addition of a little zinc solution have any effect. If, then, 0.1 *M* ferrocyanide solution is added dropwise the solution, after several drops have been introduced, slowly turns grey, then violet. Obviously, a certain quantity of $K_2Zn_3[Fe(CN)_6]_2$ precipitate must be present before the indicator responds to the ferricyanide. If, however a considerable quantity of zinc sulfate is present right from the beginning, ferricyanide produces a blue color within a few seconds, even in the absence of the ferrocyanide precipitate [compare (28)]. In analogous experiments, *diphenylamine sulfonate* exhibited a much more sluggish response, which leads to the conclusion that it would not be suitable for this titration. Actual trials confirm this prediction.

Kolthoff proved that a potassium ferricyanide solution containing sulfuric acid will no longer turn blue with diphenylamine if 0.01 mole ferrocyanide is present per mole of ferricyanide. He further observed that the discharge of a blue ferricyanide solution on the addition of ferrocyanide is very slow if no zinc-ferrocyanide is present. In pure ferricyanide solution the color depends on the concentration.

Compare in this connection the statements of Someya regarding the titration of ferricyanide, p. 179.

Further Possibilities of Using Diphenylamine, Diphenylbenzidine and Diphenylamine Sulfonate as Indicators in Redox Titrations

(a) *Titrations with Bichromate, Ferricyanide and Vanadate as Oxidizing Agents*

Someya (15, 16, 17, 23) found that with diphenylamine as indicator Ti (III), Cr (II), U (IV), U (III) and Cu (I) salts, in proper acid concentrations, can be directly titrated with bichromate. The disagreement between his statements relative to U (IV) and U (III) and those of Kolthoff and Lingane (47) is probably due to the different acid content of the solutions.

Someya found that diphenylamine is also suitable for the titration of ferricyanide, in sufficiently strong hydrochloric acid, with titanous or stannous solution. In addition, it may be pointed out that Lang and Gottlieb (58) titrated molybdenum (V) with vanadate solution in the presence of diphenylamine sulfonate.

(β) *Titrations with Ceric Salt as Oxidizing Agent*

The use of *diphenylamine* and *diphenylbenzidine* in *titrations* of *ferrous solution with ceric sulfate* solution was tested by Willard and Young (29). In the *presence of phosphoric acid,* the end point was very sharp and, provided the hydrochloric acid concentration was not too great, even when trivalent iron was previously reduced with stannous chloride in the usual manner. However, the color change was very sluggish when an excess of ceric salt was titrated back with ferrous sulfate solution.

The *procedure* was: 0.3 g. of iron was dissolved in 5 cc. of hydrochloric acid (sp. gr. 1.18), reduced with stannous chloride, the solution diluted to 150 cc., 7.5 cc. of phosphoric acid (sp. gr. 1.75) added and then various volumes of hydrochloric acid. The indicator used (1% solution) is stated in the following:

Under these conditions, when 0.8 cc. of diphenylamine or diphenylbenzidine solution was employed, there was a constant error of —0.2 to —0.3 mg. of iron, and even when 30 cc. of hydrochloric acid (sp. gr. 1.18) was added later. The error was eliminated if the test was made in an atmosphere of carbon dioxide. Accordingly, under such circumstances, the indicator error disappears.

When 1.6 cc. or 3.2 cc. of *diphenylbenzidine* was used the error remained about the same, but the color change was not so sharp. But in the presence of 1.6 cc. or 3.2 cc. of *diphenylamine,* the error was 0.0 to +0.8 mg. of iron, therefore the values are markedly higher.

Willard and Young prefer diphenylamine to diphenylbenzidine, because the latter's slight solubility may easily cause the solution to be turbid.

Lang (51) found that *ceric solution can be titrated with ferrous solution* in the presence of diphenylamine without difficulties if the solution contains enough metaphosphoric acid.

Furman has discussed this topic in Part II of this book, which deals with titrations with ceric sulfate.

(γ) *Titrations with Permanganate*

The use of diphenylamine in permanganate titrations is important only in special cases, since ordinarily the intense color of the permanganate serves to indicate the end point. Furthermore, there are available for such titrations in which the excess of permanganate is less readily detected, the very stable o-phenanthroline-ferrous salt (see p. 190) and the triphenylmethane dyes that far excel diphenylamine with respect to the color change, even though they are not so stable toward permanganate. These will be discussed presently.

Potassium permanganate, whose oxidation potential is higher than that of bichromate and of about the same order of magnitude as that of ceric sulfate, may, even at low concentrations, exert an oxidizing action on diphenylamine. Kolthoff [(121) vol. II, p. 284] found that a solution, which was at least 0.4 N with respect to sulfuric acid and that contained 0.05 to 0.4 cc. of 0.1 % indicator solution per 100 cc., was colored distinctly violet by as little as 0.04 cc. of 0.01 N potassium permanganate solution ($KMnO_4$ concentration $= 4 \times 10^{-6}$ N). The color lasted 5 minutes. The sensitivity of the indicator does not change when hydrochloric acid is present, but is considerably less in neutral solution ($KMnO_4 = 1 \times 10^{-5}$ N). In comparison Kolthoff gives the following figures for sensitivity of the self-color of permanganate:

0.1 cc. of 0.01 N $KMnO_4$ in 100 cc. gives an extremely pale color ($KMnO_4$ concentration $= 1 \times 10^{-5}$ N).

0.2 cc. of 0.01 N $KMnO_4$ in 100 cc. gives a pale violet ($KMnO_4$ concentration $= 2 \times 10^{-5}$ N).

Temperature and acid concentration are without effect.

Accordingly, diphenylamine can be recommended as indicator for titrations with permanganate when very dilute solutions are involved.

Scott (11) suggests the use of diphenylamine in the ordinary iron titration following the reduction of trivalent iron with stannous chloride.

Diphenylamine can not be used in the extremely important oxalic acid titration because the permanganate reacts with diphenylamine much more rapidly than with oxalic acid and the latter reduces the indicator only very slowly.

It is worthy of mention that Mn (III) in complexes with metaphosphate or fluoride ion can be titrated with ferrous solution in the presence of diphenylamine (35, 41, 55).

SECTION II

Erioglaucin, Eriogreen, Setoglaucin and Related Compounds

A second group of indicators important for volumetric determinations consists of erioglaucin, eriogreen, setoglaucin and related compounds. These *triphenylmethane derivatives* are quite reversible redox indicators. Their use for this purpose was suggested by Knop (59, 60, 62, 63).

He systematically tested most of the triarylmethane dyes as to their behavior toward extremely small quantities of permanganate in acid solution, and found 25 dyes that satisfactorily meet the demands as to color change and stability toward permanganate. It turned out that all the dyes that are usable as redox indicators are *diamino- and triamino derivatives* of the triarylmethane group. The oxy-derivatives exhibit a decidedly less sharp color change on the addition of permanganate.

Knop made a very thorough study of these dyes with reference to their optical, chemical and electrochemical behavior. Of these 25 dyes, he found 12 that are quite superior to the other 13 in their resistance to oxidizing agents and therefore primarily worthy of consideration for volumetric application. They are listed here by name; details as to their trade names, source of supply and number in the dyestuff tables are to be found in (62).

Acronol brilliant blue
Cyanin B
Cyanol fast green 2G
Erioglaucin A
Eriogreen B
Patent blue A
Setocyanin supra
Setoglaucin O
Setopalin conc.
Xylene blue AS
Xylene blue VS
Xylene cyanol FF

General Properties of the Triarylmethane Redox Indicators

The *color change* of the indicators just listed is very striking: it occurs in acid solution (acid concentration about 0.4 to 1.2 *N*) from yellow or green to orange or pink (in some cases bluish red). The transition interval is narrow, the change is sharp and the reversibility good, in some cases very good The response of some is rather sluggish, a fault shown by other redox indicators (see diphenylamine, etc.).

Knop defined the colors more exactly by giving the wave lengths of the characteristic absorption bands before and after the transition. He also gave a short description of the absorption spectra [(59) p. 114].

From these photochemical findings he tried to gain an insight into the *chemical action at the color change.* As yet, he has been able to establish only that the transition essentially is not a change of the triarylmethane derivatives into benzidine derivatives. This reaction can enter only as a *side reaction* that can be detected by the fact that the end color does not persist but reverts more or less quickly, and that repeated oxidation and reduction of the dye solution causes the change to become progressively weaker and finally to disappear, that is, the original dyestuff is gradually destroyed. (In comparison to diphenylamine, the destructive side reaction is much greater.)

In addition, Knop, with the aid of the iron-permanganate reaction, determined the *transition potentials* of the indicators [(62) p. 265]. The following table gives the values within 0.01–0.02 volt for the 12 best dyes, in a solution that was 1.3 *N* with respect to sulfuric acid and 1/60 *N* with respect to ferrous sulfate. The values are referred to the normal calomel electrode.

TABLE VII

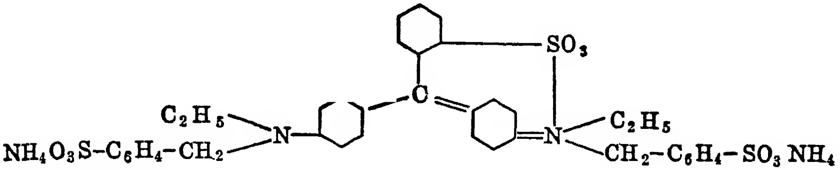
Indicator	Transition Potential (volt)
Xylene blue VS	+0.81
Setopalin conc.	+0.78
Cyanol fast green 2 G	+0.75
Xylene blue AS	+0.74
Acronol brilliant blue	+0.73
Cyanin B	+0.73
Eriogreen B	+0.72
Setoglaucin O	+0.72
Xylene cyanol FF	+0.71
Patent blue A	+0.71
Erioglaucin A	+0.71
Setocyanin supra	+0.71

Closely connected with this height of the transition potential is the observation that these indicators, in contrast to diphenylamine, respond only to oxidizing agents with the strength of permanganate, while they are *insensitive to bichromate* and also therefore to *ferricyanide* and *ferric salts.* On the other hand, they are much more liable to destruction by oxidizing agents, which action may, in some cases, be promoted by intermediate reactions during the titration (see p. 185). Therefore when an oxidizing agent such as ceric sulfate is to be titrated with ferrous sulfate it is absolutely necessary to introduce the indicator just prior to the change.

The *ready solubility* of these triarylmethane indicators *in water* is a great advantage. Knop always uses *0.1% aqueous solutions.* These show no deterioration on standing. For a titration he adds enough indicator to distinctly color the solution, in general *0.5–1 cc.* is about correct.

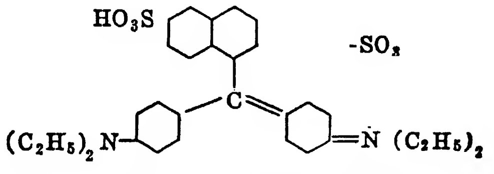
The three Knop indicators that have been most used will be described in some detail.

Erioglaucin A, according to Knop, has the structural formula:



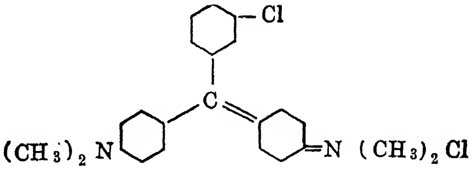
The water solution is blue. In the presence of considerable mineral acid, the yellow polyacid salts of the dye are formed, while solutions that are not too strongly acid take on the green of the mixture. On the addition of only 0.3 cc. of 0.01 N potassium permanganate to a mixture of 400 cc. of 0.4 N sulfuric acid and 1 cc. of indicator solution, the green turns toward red ($KMnO_4$ concentration $= 1 \times 10^{-5}$ N). With 0.1 cc. of 0.01 N KMnO a light grey transition shade appears ($KMnO_4$ concentration $= 3 \times 10^{-6}$ N). The original green is immediately restored by a small addition of ferrous sulfate solution. The sensitivity may be even higher in titrations, possibly because of intermediate reactions.

Eriogreen B has the structural formula:



It dissolves in water to form a blue green solution. An intense yellow appears when only a little acid is present. A sharp change to orange yellow follows the addition of 0.1 cc. of 0.1 N permanganate to a mixture of 2 cc. of eriogreen solution and 400 cc. of 0.4 N sulfuric acid ($KMnO_4$ conc. $= 3 \times 10^{-6}$ N). A little ferrous sulfate solution causes the original yellow to reappear. The *transition is delayed considerably,* so that at the end point of the titration it is necessary to wait for a few seconds after each addition of the titrant. As a compensation, eriogreen is *much more resistant* to the destructive action of permanganate than erioglaucin and setoglaucin, for instance; a fact that is apparent from the greater permanence of the transition color.

Setoglaucin O was recommended by Knop for titrations in solutions containing *hydrochloric acid,* and especially for iron after reduction with stannous chloride, because this indicator, under these conditions, proved far more stable than eriogreen (see, however, p. 185). Setoglaucin has the structural formula:



The aqueous solution is deep blue. In sulfuric acid solution the transition is like that of erioglaucin: from green through yellow to yellow red; in hydrochloric acid solution the color goes from yellow to yellow red.

Use of Redox Indicators of the Triarylmethane Group

The Titration of Iron with Permanganate

By means of potentiometric titrations, Knop showed that the *potential* at the *equivalence point* of the iron-permanganate reaction (0.73 volt) practically coincides with the *transition potential* of the 12 most serviceable indicators (see p. 182). Additional experiments confirmed this finding.

The *titration* of quantities of iron equivalent to about 20–40 cc. of 0.1 *N* solution is made in the customary way. The solution should contain 0.5–1 cc. of indicator solution per 100 cc. and at the end of the titration should be roughly 1 *N* with respect to sulfuric acid. Toward the end of the titration, the permanganate should be added in small amounts and it is advisable to wait a few seconds after each addition, since otherwise there is considerable danger of over-titrating. The end point has been reached when the color change persists for at least 15 seconds; it can be hit quite closely with even 0.005–0.01 g. of 0.1 *N* permanganate solution.

To obviate, as much as possible, the *destruction of the indicator through oxidation,* it is advisable not to add too much of the titrant at one time and to shake thoroughly and continuously. Such dropwise titration (size of drops = 0.01 cc.) with mechanical stirring, gave Knop the same permanganate consumption in the presence of the best indicators as did the usual iron titration without an indicator. These latter figures were corrected by subtracting 0.01 cc.

The writer has found that in titrations conducted in the usual way, considerable and variable *corrections* of the permanganate consumption must be reckoned with, even though the titrations are made with great care. This was proved by comparing the results of adding the indicator at the *beginning*, with those obtained when the indicator was introduced toward the *end* of the titration. Table VIII gives the results in per cent content of Mohr's salt; each value is the average of several parallel trials.

TABLE VIII

Indicator	Indicator Added		D
	At the beginning	Near the end	
Setoglaucin	100.21	99.82	0.39%
Erioglaucin A	99.93	99.84	0.09%
Eriogreen B	99.89	99.82	0.07%

The surest method of obviating any considerable correction is to carry the titration first to the usual end point of the reaction without an indicator; then a few drops of a known solution of ferrous salt are added and the final titration made with an indicator present. An excellent *direct determination of the indicator correction* for this type of procedure can be made *empirically:* A pure ferric solution is treated with sulfuric acid and manganous sulfate in such quantities that their concentrations will be the same as those at the equivalence point. The indicator is added, and the solution titrated with small portions of 0.1 *N* permanganate solution (weight burettes were used exclusively) until a color change lasting at least 15 seconds is obtained. About 0.015 cc. of 0.1 *N* permanganate solution was required with these three indicators. If the back-titration is carried back and forth, this figure may easily be raised to 0.02 and 0.03 cc., the increase being much more rapid with erioglaucin than with eriogreen.

Titrating in the presence of an indicator has the advantage over the usual method in that the *sharpness of the change is hardly decreased in poor or artificial light.* The end point of the reaction can be detected without difficulty even *in hydrochloric acid* solution with *no phosphoric acid present;* the greater destruction of the indicator during the titration must be kept in mind, of course. The addition of 10 cc. of Zimmermann-Reinhardt solution is not sufficient to prevent this side reaction. Knop obtained satisfactory results with eight of the indicators by *adding 10 cc. of 20% manganous sulfate solution* to 100 cc. of iron solution containing 10 cc. of concentrated hydrochloric acid. The deviations from the values obtained in the presence of Reinhardt solution but with no indicator, still amounted to +0.1 to +0.4% when about 30 cc. of permanganate was used. In these experiments *setoglaucin* gave the smallest over-consumption. Since mercuric chloride and stannous chloride have no appreciable effect on the indicator, ferric salt, *after reduction with stannous chloride,* can be titrated in the presence of setoglaucin. In this case also, the indicator error is only about 0.1%.

It must be noted that in the iron titration in hydrochloric acid solution, certain indicators *do not reassume the original color in the back-titration.* For instance, the yellow red of setoglaucin reverses to a bluish green rather than to yellow. The transition, however, is improved by this. Knop found that both in sulfuric and in hydrochloric acid, the acid concentration of the iron solution may depart considerably from the quantities prescribed above. However, larger quantities of hydrochloric acid lessen the sharpness of the color change.

Indicators are of particular significance when iron is titrated in the presence of highly colored ions such as nickel and cobalt. An indicator of suitable color and concentration can be selected according to the kind and quantity of the foreign salt. Knop was able to determine 0.1 g. of iron within 1 to 2 parts per thousand in the presence of 3 g. of nickel or 1 g. of cobalt.

Knop, in collaboration with Kubelkova (63), made an intensive study of the applicability of the indicators to the *micro-titration of iron* with permanganate. They succeeded in developing a procedure which permits the determination of 1 mg. of iron within 0.1%, either in sulfuric or hydrochloric acid solution. The error could be brought down to 0.2–0.4% even with samples containing as little as 0.1 mg. of iron.

The Titration of Potassium Ferrocyanide with Permanganate

The titration of potassium ferrocyanide is made considerably easier by the use of *erioglaucin* and *eriogreen.* (The other triarylmethane indicators have not yet been tested for this titration.) The titration is made in the customary way without any special precautions beyond taking due account of what has already been said about these indicators. The end point is excellent; according to Knop, it may be determined within

0.02 cc. of 0.05 *N* potassium permanganate solution. The writer has found that for *eriogreen, the correction* is 0.007–0.011 g. of 0.1 *N* potassium permanganate, as determined in a pure solution of potassium ferricyanide containing sulfuric acid. This accuracy makes it possible to use potassium ferrocyanide of known composition as primary standard for permanganate solutions, especially for dilute solutions [see also (64)].

The slighter resistance of these indicators to the oxidizing action of permanganate [(59) p. 121] makes itself evident if *hydrochloric acid solutions* are used. For this reason, *erioglaucin A* cannot be employed. With *eriogreen B,* however, there is obtained a very *constant over-consumption* of 0.1–0.15 cc. of 0.05 *N* permanganate solution. This may be regarded as a correction, unless it is preferred to standardize the permanganate solution against ferrocyanide, maintaining the same conditions—especially the same consumption of the titrant.

Kolthoff and Sandell (37) have given a brief discussion of the titration of *arsenious acid with permanganate* in the presence of *eriogreen B* and *setopalin.*

The Titration of Ferrous Sulfate with Ceric Sulfate

Furman and Wallace were the first to test the behavior of erioglaucin and eriogreen in the titration of ferrous solution with ceric sulfate. They found both indicators to be quite good for this case. For details see Furman, Part 2 of this book, page 37.

SECTION III

TRI-ORTHO-PHENANTHROLINE-FERROUS SULFATE†

Walden, Hammett and Chapman (65, 66) introduced ortho-phenanthroline-ferrous solutions and thereby provided volumetric analysis with a quite reversible redox indicator that can be used for many purposes. This is a new type of indicator because it is a metallo-complex salt, whereas the indicators discussed previously are purely organic compounds.

Blau (117) while studying the nature of the intensely red compound produced when α,α′-dipyridyl and ferrous salt are brought together, made, for the first time, o-phenanthroline (also called α-phenanthroline). He observed that this also forms very stable red ferrous complex salts "which are the most perfect analogues imaginable of the tripyridyl-ferrous salts." He determined the structure of these salts and made a thorough study of their properties.

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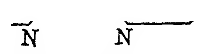
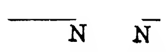
† Gleu (68) proposes for this the name Ferroïn; correspondingly, he terms the oxidation product, Ferriïn.

General Properties of Tri-o-Phenanthroline-Ferrous Sulfate

The following structural formulae show plainly the close relationship between o-phenanthroline and α,α′-dipyridyl:



o – Phenanthroline



αα′– Dipyridyl

Blau showed that only compounds of this kind, but not their isomers, are capable of forming stable, intensely colored complexes with ferrous ion. In these, 3 molecules of the organic compound enter the inner sphere around the ferrous ion as the central atom, while the anion of the iron salt remains combined as ionogen. Therefore, each diamine molecule satisfies two coordination valences. These complexes can be included among the complex hexammines. The respective formulae are:

$[Fe\ (C_{12}H_8N_2)_3]^{++}$

tri-o-phenanthroline-ferrous ion

$[Fe\ (C_{10}H_8N_2)_3]^{++}$

tri-α α′-dipyridyl-ferrous ion

According to Blau, *strong* oxidizing agents cause the *color change* (dark red to light blue) because they convert the iron to the trivalent stage, that is, they produce the ions:

$[Fe\ (C_{12}H_3N_2)_3]^{+++}$ $[Fe\ (C_{10}H_8N_2)_3]^{+++}$

Blau calls these tri-phenanthroline- and tridipyridyl-ψ-ferric ions rerespectively, since (in contrast to the ferrous compounds) they cannot be prepared by simple addition of ferric salt to the appropriate diamine, but only by oxidation of the ferrous complex. They are reduced by even very weak reducing agents, such as mercury and silver.

This simple oxidation process, together with the great stability of the complex, explains the *very excellent reversibility* of the color change and the *extraordinary resistance* of the indicator against destruction. (The indicator is not visibly decomposed even when iron is titrated in hydrochloric acid solution without the addition of manganous sulfate.) Blau found that dilute mineral acids in the cold attack the ferrous-phenanthroline complex only after long standing, while 5% sulfuric acid exerts a destructive action after a few minute's boiling. In cold 10% sulfuric acid the color of the solution fades only after hours of standing.

The *normal potential* E_{0H} (1.14 volts) of the indicator in 1 M sulfuric acid was determined by Walden, Hammett and Chapman with the aid of the ferrous-ceric sulfate titration. Since the color of the reduced stage is much more intense than that of the oxidized stage, the *color change* occurs when the oxidation is 90% complete, that is *at 1.20 volts.* The potential falls with rising acid concentration (70). These writers emphasize that this potential determined with ceric solution does not give grounds for any detailed statements concerning the utility of the indicator in titrations with bichromate or permanganate (see p. 155f).

The high transition potential is in accord with the fact that phenanthroline-ferrous solution is entirely resistant to oxidation by the air and that the change is brought about by strong oxidizing agents only.

Walden and his co-workers have given exact directions for the preparation of o-phenanthroline. A solution of the stoichiometric quantity of phenanthroline monohydrate (formula weight 198.1) *in an acid-free 0.025 M ferrous sulfate solution* is recommended for use in titrations. The solution does not change appreciably within a year. One drop is sufficient for a titration; less than 0.01 cc. of 0.1 N oxidizing agent is necessary for its complete oxidation. One drop in 200 cc. of solution gives the best color intensity.

The formation of the ferrous complex is slow and incomplete if the ferrous solution is added to a strongly acid phenanthroline solution, and does not occur at all if the latter contains other metals that form stable complexes with phenanthroline (cobalt, nickel, zinc, cadmium, copper).

Walden and his collaborators do not recommend *α,α'-dipyridyl-ferrous salt* as indicator because it is decomposed much more easily by acids than is the o-phenanthroline-ferrous salt. There is great difficulty in determining its oxidation potential.[18]

A search among the complex salts of other metals with o-phenanthroline revealed no usable indicators. However a *ferrous-nitro-o-phenanthroline complex* behaved like the parent substance, but its oxidation potential is obviously somewhat higher (53, 54).

The Use of Tri-o-Phenanthroline-Ferrous Sulfate

The Titration of Iron With Bichromate

In contrast to Blau's statement that chromic acid does not affect phenanthroline-ferrous ion, Walden, Hammett and Chapman found that this indicator can be used satisfactorily for the iron-bichromate titration.

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[18] See [(120), p. 71]; compare, however (118); see also p. 33.

The writer has confirmed this finding and in fact believes that it is *superior to diphenylamine.*

The color change is so distinct that it may be detected even without diluting (to reduce the chromic (III) color) and in the absence of phosphoric acid. It is more convenient, however, to use conditions approximating those prescribed by Knop (see p. 164). The *change* is from yellow to brownish green to bluish green. In parallel determinations, no difficulties were encountered in getting agreement within 0.05% (weight burettes), also in approximately 2 *N* sulfuric acid, or when sulfuric or phosphoric acid was replaced by hydrochloric acid or ammonium fluoride, respectively. It makes no difference whether the indicator is added at the beginning or near the end of the titration, even when bichromate is to be titrated in hydrochloric acid solution. *No indicator correction is necessary* if 0.1 *N* solutions are used. The result is practically the same as that of the titration made in the presence of diphenylamine (see p. 172).

The only noteworthy fact is that the *color change* is usually *delayed* considerably *if the final titration is made with bichromate.* Walden and his co-workers, in this case, recommend waiting a few seconds after each addition of the oxidizing agent. The writer found it safer always to *make the final titration with ferrous sulfate* solution; the change then occurs instantly even with very small increments and is quite permanent. The interval between the first plainly perceptible color change and a deep coloration amounts to about 0.01 cc. of 0.1 *N* ferrous sulfate solution.

The contradiction of these findings to those of Blau, can obviously be explained by the fact that the *color change* in the titration *is induced by the iron-bichromate reaction;* because, quite analogous to diphenylamine (see p. 165), the retardation of the color change in the presence of an excess of bichromate can be relieved by adding 1–2 drops of 0.1 *N* ferrous sulfate solution.

The Titration of Iron with Potassium Permanganate

Walden, Hammett and Chapman titrated ferrous sulfate with potassium permanganate in the presence of phenanthroline-ferrous ion. They obtained an accuracy of several hundredths of one per cent.

The *color change* was about as *sharp* as that of the tri-phenylmethane indicators, even *in poor or in artificial illumination.* It occurs with as little as about 0.007 g. of 0.1 *N* solution. The change is from a strong yellowish-red to a pale bluish-green, in case only sulfuric acid is present. On the other hand, in approximately 1 *N* hydrochloric acid solution it goes to a decided yellow ($FeCl_3$ color). In the latter case, the *color change occurs instantaneously* with either ferrous sulfate or with permanganate and *persists.* This is also true in solutions acidified with sulfuric acid if the end point is reached with permanganate, but when titrating with ferrous sulfate the first change is evanescent, and it is advisable to titrate to a change that still is easily recognized after 30–60 seconds.

Phenanthroline-ferrous ion is *far superior to the triphenylmethane indicators in resistance to destructive oxidation*; the result is independent (within 0.02%) of the time of adding the indicator, even when titrating in approximately 1 *N* hydrochloric acid solution, provided the liberation of chlorine is prevented by adding 20 cc. of 20% manganous sulfate solution (writer's unpublished experiments).

Walden, Hammett and Chapman obtained an average deviation of 0.05% in their titrations of small quantities of iron with 0.01 *N* potassium permanganate.

It is of particular interest from a practical standpoint, that because of the high oxidation potential of phenanthroline-ferrous sulfate, it is possible to titrate successively *chromium* and *vanadium* with potassium permanganate (72).

Titrations with Ceric Solutions

Since the indicator question has particular significance in the use of ceric solutions in oxidimetric titrations, Walden, Hammett and Chapman (66) as well as Willard and Young (67) tested the new indicator with this special use in mind. It meets the requirements quite satisfactorily.

In titrations, in 1 *M* sulfuric acid, of ferrous sulfate with ceric solution and also in the reverse titration, Walden and his co-workers, using weight burettes, found a maximum deviation of 0.03% in parallel determinations. The corresponding figure with 0.01 *N* solutions was 0.2%. The results, to a large extent, are independent of the concentration and the kind of acid. Lang observed, however, that the titration of ferrous salt in the presence of mercurous chloride is vitiated because the calomel adsorbs the indicator. The change occurs too late or not at all (private communication). Iron can be titrated even in the presence of vanadium (IV) in 5 *M* sulfuric acid (71).

Sodium oxalate is used to standardize ceric solutions and Willard and Young tested phenanthroline-ferrous indicator in this important titration. It proved quite good for 0.1 *N* and 0.01 *N* solutions if the titration is carried out in the presence of iodine monochloride at 45–50° C. in a solution not too strongly acid. At higher temperatures the indicator is decomposed, while the change is delayed if the concentration of the acid is too high.

According to Gleu (68) *arsenious acid* may be titrated without difficulties in the presence of sulfuric acid if several drops of 0.01 *M* osmium tetroxide solution are added as catalyst. As to the indicator transition, the observation is opposite to the behavior of diphenylamine in the ferrous-bichromate titration (see p. 166), for whereas, trivalent arsenic has no action on the oxidized indicator, the reduction product is immediately obtained, because of induced reduction, when some ceric solution is added.

Lang (51) points out that phenanthroline-ferrous ion cannot *be used* in the titration of ceric salt in the presence of metaphosphoric acid.

Details of the use of ceric solutions are given in Part II of this book.

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PART VII

ADSORPTION INDICATORS FOR PRECIPITATION TITRATIONS

BY

KASIMIR FAJANS

ADSORPTION INDICATORS FOR PRECIPITATION TITRATIONS

INTRODUCTION

Development of the Method. The editor of this volume, Wilhelm Böttger,[1] quite properly has cited the discovery of the volumetric methods employing adsorption indicators as an example of a practical procedure developed from well known observations only after their theoretical elucidation had been worked out.

The main facts underlying the first examples of titrations of silver salts and halides using dye stuffs of the fluorescein series as indicators, that is, the coloring of silver halides by these dyes to a shade different from that of the solution, as well as the dependence of the intensity of this coloration on there being an excess of silver salt or halide present in the solution, was mentioned as early as 1894 by Hübl,[2] and in 1901 by Lüppo-Cramer,[3] in connection with photographic sensitizing. These phenomena were studied in more detail by Kieser in 1904.[4] Nevertheless, these facts were not applied to volumetric analysis until much later (1923) when they were observed again by Fajans and Hassel (1), who called attention to them in connection with the ideas then newly developed[5] concerning the mutual change (deformation) of the electron systems and the concomitant changes in optical properties of closely adjoining ions. These facts were also linked with certain views regarding the adsorption of ions on polar precipitates.[6]

The argentometric halide titrations, described by Fajans and Hassel, in which fluorescein and eosin were used as indicators, were worked out in greater detail by Fajans and Wolff (3) and extended to a larger number of fluorescein derivatives and to dye stuffs of other classes including basic ones,[7] especially rhodamine 6 G. Böttger and Schmitt[8] were the first to check the new method.

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[1] Böttger, Acta chemica Fennica Nr. 1-2 (1930).

[2] v. Hübl, Eder's Jahrbuch, 1894, p. 189.

[3] Lüppo-Cramer, Arch. wiss. Phot. *2*, 277 (1901).

[4] Kieser, Dissertation, Freiburg i. Br. 1904.

[5] Fajans, Naturwissenschaften *11*, 165 (1923).

[6] Fajans and v. Beckerath, Zeit. phys. chem. *97*, 478 (1921).

[7] Hodakow (37) unaware of the work of Fajans and Wolff suggested the basic dyes, methyl violet and crystal violet.

[8] Böttger and Schmitt, Zeit. anorg. allg. Chem. *137*, 246 (1924).

Several advances, such as the discovery of the singular case of phenosafranin as indicator (compare p. 230) and the extention of the method to the titration of lead and chromate (compare p. 238) can be found in the Munich Dissertation of Weir (1926). The further development of the method along practical lines has been the valuable contribution of Kolthoff who, with several co-workers,[9] since 1927, has compared the accuracy of the new methods with that of the older procedures. He suggested several improvements and also additional indicators. The new method is discussed in detail in his book, "Die Massanalyse" (25). Kolthoff coined the appropriate name "adsorption indicators."

In recent years valuable contributions to the development of the methods employing adsorption indicators have come from various sources. See p. 233 ff. or the Bibliography for the pertinent references.

Principle of the Method. Adsorption indicators are used in precipitation analyses, that is, their application assumes that in the course of the titration there will be formed a difficultly soluble compound of the type AB. The new type of indicators, in common with those previously used for such analyses, under the influence of the precipitant B, undergo at the equivalence point a change of condition accompanied by a change of color.[10] However, with the other type of indicators this change is due to a reaction between the indicator (I) and the precipitant forming either (a) an undissociated compound, BI, *in the solution*, (for example, $Fe(CNS)_3$ in the Volhard silver determination) or (b) a precipitate of a slightly soluble compound, BI, whose *solubility product has been exceeded* (for instance Ag_2CrO_4 in the Mohr determination of chloride). In contrast, the change of the adsorption indicators occurs on the surface of AB. In all the cases that have been studied closely, with one exception,[11] the change of the condition of the adsorption indicator is linked with its passage out of the solution onto the surface, that is, with its adsorption on AB, or with the reverse process of desorption.[12] The action of the precipitant at the equivalence point consists in a considerable increase in the degree of adsorption, that is, as in (b) in a removal of the indicator from the solution *without*, however, *the solubility product*

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[9] See the bibliography on p. 247.

[10] The indicator is taken to be only that part of the indicator which participates in the color change. No account is taken here of its electrical condition.

[11] The titration of halides with silver nitrate in the presence of phenosafranin as indicator, compare p. 231.

[12] The theoretical discussion will deal chiefly with adsorption which occurs more frequently in practice than desorption.

of BI being exceeded. This difference can be shown by the titration of a highly dissociated bromide (Br^-) with a silver salt (Ag^+) and eosin as indicator. The explanation can be comprehended easily if the following facts are kept in mind.

1. A sol or precipitate of AgBr in the presence of an excess of Br^- or Ag^+ adsorbs these ions from the solution and is present as negatively charged bromide body $[AgBr]\ Br^-$ or as positively charged silver body $[AgBr]\ Ag^+$.
2. The negatively charged eosin anion is not adsorbed appreciably by the bromide body but is strongly adsorbed by the silver body.
3. The eosin anion when adsorbed on silver bromide exhibits a different color than when in solution.

These facts, as well as the principle of the new titration method, are nicely shown by the following *demonstration experiment:*[13]

Two beakers, each containing 1 liter of an aqueous solution of about $\frac{1}{300}$ g. of sodium eosinate, are placed side by side. (The concentration of this solution is approximately 5×10^{-6} molar). At this dilution the salt is extensively ionized; the yellow-red transmitted color and the greenish fluorescence are due to the free eosin anions. If to one of the solutions (the other serves merely for comparison) there is added from a burette about 5 drops (each approximately 0.06 cc.) of 1 *N* silver nitrate solution, no change in the color of the eosin will be perceived.[14] At this great dilution the slightly soluble silver eosinate obviously remains dissolved and dissociated. If now, to this solution, there is added from a second burette, 1 drop, that is, a deficit, of 1 *N* potassium bromide solution, there will be observed a strong deepening and change of the color toward red, as well as a decrease of the fluorescence. What has happened? Silver bromide has been formed and since the solution has remained perfectly clear the precipitate evidently is present in the colloidal form with a great development of surface.[15] Since the solution contains an excess of silver ions, the sol particles form a positively charged silver body; this adsorbs the negative eosin anions and the latter undergo a change in color and a loss of fluorescibility. That this is true can be shown easily by continuing the experiment. When additional (2–3 drops) potassium bromide is added, the red color becomes still darker because the quantity of silver bromide and therefore the quantity of adsorbed dye is increased. When 4 and especially 5 drops[16] are added the color of the solution again becomes lighter, because the concentration of the excess silver ions and therefore the intensity of the positive charge of the silver bromide is diminished. This results in a decrease in the adsorption of the eosin anions. With 6 drops of potassium bromide, that is, when the equivalence point has been passed, the solution regains its original yellow-red color and the fluorescence of the free eosin ions: due to the excess of potassium bromide the negatively charged bromide body is now present, the eosin ions are displaced from the surface and return into the solution. Now by adding alternately silver nitrate and potassium bromide, the color play can be repeated at will; by producing the positive silver body the dye can be brought onto the surface, or it can be removed if the bromide body is formed.

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[13] Compare (1) and (2).

[14] If a distinct shift of the color toward red follows, it indicates that the water used in preparing the eosin solution contained chloride. This color reaction is a much more sensitive test for halide ions than the turbidity produced by adding silver solution (without eosin).

[15] The adsorbed dye aids in preventing the coagulation of the colloid.

If the quantity of precipitated silver bromide is increased, the solution gradually becomes turbid, but the color changes, just described, can be observed in the presence not only of larger quantities of a sol but also of a flocculated precipitate of silver bromide; the color can be observed either on the surface of the precipitate or in the supernatant sol which has not yet flocculated. These are the conditions under which the titrations are normally conducted, since usually the solutions are considerably more concentrated than those used in this demonstration experiment. However, in all cases, the essence of the phenomena is the same.

The phenomena that determine the action of the adsorption indicators will now be discussed in more detail.

THEORY OF THE ADSORPTION INDICATORS

General Considerations Concerning the Adsorption of Ions on Polar Adsorbents. Several ideas concerning the adsorption of ions on materials possessing a polar structure will be developed first. These concepts have been found very useful in the origination and development of the method, and the experimental facts can be understood better with their aid.

The substances used as adsorbents and obtained by the precipitation of an ion with another of the opposite sign do not usually form typical ionic lattices. These sparingly soluble materials represent transition cases between this heteropolar type of binding and either, as in the case of the silver halides, the covalent atomic lattices or, as does silver sulfide, the metals.

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[16] Under the conditions of the experiment, the eosin ions are adsorbed only weakly by the "equivalent body" of the silver bromide (compare p. 211). For details see p. 222.

However, the polar contrast between the original ions in the adsorbents in question is sufficiently marked so that the behavior of the adsorbents can be ascribed to a large degree to electrostatic forces. It is therefore permissible in order to picture the lattice and its surface to refer, with the above reservation, to the representation of an ionic lattice. The growth of a crystal of this kind from a supersaturated solution may be imagined as due to the ions on the surface of the lattice each taking up an ion of opposite charge. This mechanism can also be assumed for the adsorption of ions, both for the ions of the lattice itself as well as for foreign ions, in so far as the latter involves an *addition adsorption.* If the adsorbent is in contact with its saturated solution, either in pure water or in an electrolyte solution, in general different amounts of the partially dehydrated positive and negative ions of the solution will be taken up on the surface. Depending on whether an excess of positive (compare Figure 1*a*) or negative (*b*) ions is adsorbed in this manner, the surface of the precipitate acquires the corresponding charge and attracts the oppositely charged ions together with their hydrate envelope, which acts as the intermediate medium of the Helmholtz double layer that is developing.

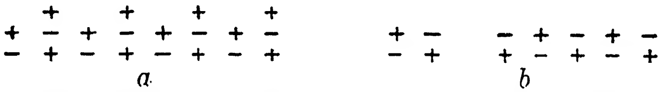

FIG. 1 Schematic representation of a polar lattice that is electrically charged by adsorption of ions from a solution: in *a* positively (silver body, for example), in *b* negatively (halide body, for instance).

In accordance with this conception, *both* ions of the dissolved electrolyte are concentrated in the interface, even though by different means. If the following discussion involves principally the adsorption not of the salt but of *one* ion (for instance, the eosin ion) this is because, in most cases, the decrease of the concentration in the solution has been determined experimentally for this ion only, and secondly, because the forces between this ion and the surface are chiefly responsible for the accumulation in the double layer, while the other ion of the salt (Na^+) participates only for reasons of electroneutrality.

There are cases in which actually only one of the ions of the dissolved electrolyte accumulates in the surface and electroneutrality is maintained by an ion of like charge leaving the surface layer and entering the solution.[17] Kolthoff and his co-workers [18] have shown that this *exchange adsorption* plays an important part also in the adsorption of dye stuff ions. For instance, when fluorescein is adsorbed on silver chloride, chloride ions are given up to the solution. Kolthoff assumes that this is a replacement of the chloride ions of the lattice itself by fluorescein ions,[19] whereas Verwey (54) explains these important observations by means of processes occurring within the double layer.

It would be of interest from a theoretical standpoint to determine the part played by these types of adsorption in the various cases of titration. The following discussions are based principally on the idea, applied by the writer, of an *addition* of the dyestuff ions to the lattice surface, but the conclusions, in all essentials, are independent of this (compare, however, p. 218).

The adsorbability [20] of various ions on the adsorbent in question is of great significance in the following discussion. As to the ions of the lattice itself, its slight solubility can be viewed from the standpoint that its own ions, even at extremely low concentration, are taken out of the solution and held on the surface, and at least when comparing analogous materials it may be expected that, in general, the ions of the less soluble adsorbent will have the greater adsorbability.

The adsorption of these ions of the difficultly soluble substance itself can actually be detected by various methods. For instance, the negative charge of silver iodide against its saturated solution in pure water [21] shows that it adsorbs I^- ions more strongly than Ag^+ ions, that is, the iodide ions are at least detectably adsorbed from a solution whose concentration is only about 1×10^{-8} mole per liter. Furthermore, if in the precipitation of potassium chloride with silver nitrate the solution contains an excess of silver nitrate (or potassium chloride) the silver chloride is charged positively (or negatively) with respect to its solution; a fact observed first by Lottermoser.[22] In the first case the solution contains Ag^+, K^+, NO_3^- ions, in the second, Cl^-, NO_3^-, K^+. It is therefore natural to assume that the charge in both cases is conditioned by the adsorption of the ions of the slightly soluble lattice itself, that is, of Ag^+ or Cl^-.

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[17] For particulars see Freundlich, Colloid and Capillary Chemistry, 3rd German Ed., translated by Hatfield, p. 204. New York, 1926.

[18] Kolthoff and Rosenblum, J. Am. Chem. Soc. *55*, 2664 (1933); also (21)–(24).

[19] That this replacement of the lattice ions by the adsorbed ions is not generally responsible for the adsorption of the dye stuff ions, as Kolthoff assumes, is indicated by the existence on the surface of areas of varying addition capacities (compare p. 225, footnote 50), and follows clearly from the behavior of chromotrope F4B when adsorbed on the equivalent body or on the silver body of silver iodide, as described on p. 218.

[20] The constant $\alpha\beta$ of the Langmuir equation given on p. 210, footnote 26, can serve above all as a measure of the adsorbability. In the comparison of two analogous dyestuffs shown in Figure 3, a higher saturation value α corresponds also to a larger $\alpha\beta$.

[21] Compare Lange and Crane, Zeit. phys. chem. (A) *141*, 225 (1929); Verwey and Kruyt, ibid. *167*, 149 (1933); compare also (54).

The connection between low solubility and adsorbability can be generalized to include also the adsorption of foreign ions as shown by the studies of Paneth (1914), Fajans (since 1913), O. Hahn (since 1926) and their co-workers.[23] The regularities can be stated as follows:

The adsorbability of analogous ions increases with decreasing solubility or dissociability of their compound with the oppositely charged ion of the adsorbent.

Analogous ions in this sense are

$$Cl^-, Br^-, I^-$$

and the anions of fluorescein, eosin, erythrosin, etc. In both series the solubility of the corresponding silver salts decreases from left to right (compare Table 2).

On pages 210–214, the adsorbability [24] of the anions in these two series will be compared, and on page 220 f. the mutual effect on the adsorption of the members of both series will be discussed in more detail.

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[22] Lottermoser, Journ. prakt. Chem. [2] *72*, 39 (1905); *73*, 374 (1906).

[23] A review of the development of this question and detailed references to the literature are given in the papers of Fajans and Erdey-Grúz (4). Compare also Hahn, Zeit. Elektrochem. *38*, 511 (1932); compare King and collaborators, J. phys. Chem. *37*, 663, 851, 1047 (1933).

[24] A series of adsorption studies carried out, since 1924, in the Laboratory for Physical Chemistry at Munich, have furnished a clearer interpretation of the observations on which the new titration method is based (compare the bibliography). In the dissertations of Wolff (1924), Pohl (1924), Dehio (1926) and Weir (1926), the adsorbents were used in the condition in which they are produced in the titration, that is, as colloids, or as freshly prepared precipitates. Results that are more easily reproduced are obtained, of course, if powdered preparations having a definite surface are used. The measurements carried out thus by Walker (1927), Ketterl (1931), Schneller (1931), Pruckner (since 1934), and Van Artsdalen (1936) are the basis of the diagrams given in the text. In using these later results for developing the theory of these titrations, it will be kept in mind that the surface development of the powders is less than that in the titrations (compare Section 4). Compare also the valuable study of Hodakow (37) carried out without knowledge of the first Munich investigations. See also Sheppard and Crouch, Journ. phys. Chem. *32*, 750 (1928).

Comparison of the Adsorbability of Dyestuffs. In the first place, it will be shown that erythrosin is adsorbed much more strongly by silver iodide and silver bromide than is eosin.

The general character of the relation between the absolute quantity (a) of a material taken up by a definite amount of an absorbent and its equilibrium concentration (c) in the solution is shown by curve A of Figure 2. At very low concentrations,[25] a increases proportionately with c, then the increase becomes less steep and at sufficiently high values of c a limiting value of the adsorbed quantity is reached. This indicates a saturation of the surface with the adsorbate.[26] Correspondingly, as curve

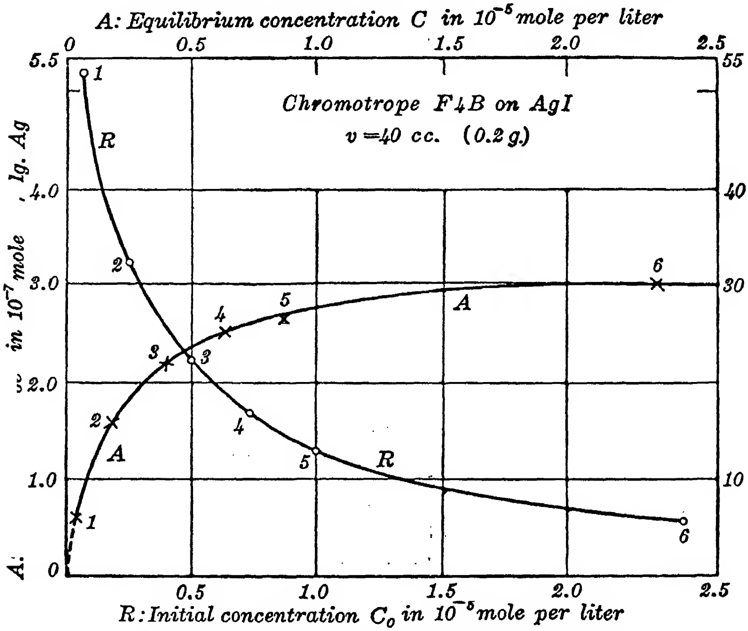

FIG. 2 Adsorption of Chromotrope F4B on AgI

Curve A. Dependence of the absolute quantity adsorbed on the equilibrium concentration C (adsorption isotherm).

Curve B. Dependence of the fraction adsorbed (%) on the initial concentration C_0.

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[25] Point 1 corresponds to $c_0 = 5.2 \times 10^{-7}$ mole per liter (compare Figure 7).

[26] The whole course of this curve is satisfactorily expressed by the Langmuir equation:

$$a = \frac{\alpha\beta c}{1 + \beta c}$$

The product of the two constants α and β determines the steepness of the rise that is linear at first (for $\beta c \ll 1, a = \alpha\beta c$), while $a = \alpha$ (for $\beta c \gg 1$) corresponds to the saturation value. For details, see Freundlich, Kapillarchemie, Volume 1, p. 191 (1930). For the curve *A*, $\alpha = 3.18 \times 10^{-7}$ mole per 1 g. AgI, $\beta = 5.93 \times 10^{-5}$ (mole/liter)$^{-1}$. ($\ll$ = much

R shows, the fraction of the total quantity of adsorbate that is actually adsorbed decreases with increasing initial concentration, c_0. Obviously, increasing the quantity or, more strictly speaking, the surface of the adsorbent, for instance by increasing its degree of dispersion, would favor the adsorption.

Figure 3, constructed from measurements made by Pruckner (13), presents a direct comparison of the quantities of eosin and erythosin adsorbed on the "equivalent body"[27] of silver iodide because they refer to the same silver iodide powder. As can be seen, the adsorbed molar quantity is greater for erythrosin than for eosin over the whole concentration range. This also holds for the saturation region where the quantities adsorbed, expressed as 10^{-7} mole of dye per gram of silver iodide, are in the relation of 17.4 : 4.3.[28]

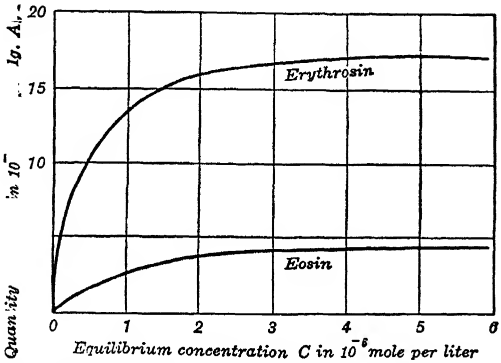

FIG. 3 Adsorption of eosin and erythrosin on AgI (0.1 g.) V = 40 cc.

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[27] *Equivalent body* denotes a system made up of an adsorbent and its saturated solution containing equivalent quantities of the oppositely charged ions of the adsorbent. The powders used for the adsorption experiments were brought as close as possible to this condition by thoroughly washing and drying the precipitated material. Since, according to Verwey and Kruyt (page 208) the preparation obtained by washing silver iodide contains excess hydrogen iodide in the double layer (represented symbolically $|\ AgI\ |\ I^- \ \vdots\ H^+$) an equivalent body can be obtained in this way only if the HI is removed completely in drying. The uncertainty in this and similar cases is emphasized where necessary by placing quotation marks around "equivalent body."

[28] It seems surprising that the adsorption capacity of silver iodide differs so greatly for two materials as similar as eosin and erythrosin. This may be due to the fact that different parts of the surface do not have the same addition capacities (compare p. 225, footnote 50), a fact which can be deduced in the case of silver iodide from the negative charge of the equivalent body. Such excess iodide ions can be displaced much more easily by erythrosin than by eosin (compare page 221). Walker (10) found almost the same saturation value (compare Figure 4 C) for eosin as for erythrosin on the silver body of silver bromide.

Erythrosin is also adsorbed considerably more strongly than eosin on the equivalent body of silver bromide.[29] This can also be regarded as a confirmation of the rule given above, because the solubility of the compound of the erythrosin ion with the oppositely charged ion of silver iodide or silver bromide is about 50 times less than that of silver eosinate (compare Table 2).

Comparison of the Adsorbability of the Halide Ions. The *adsorbability of halide ions* may be compared by a method based on the effect on the adsorption of small concentrations of materials that are easily determined, such as radioelements or dyestuffs.

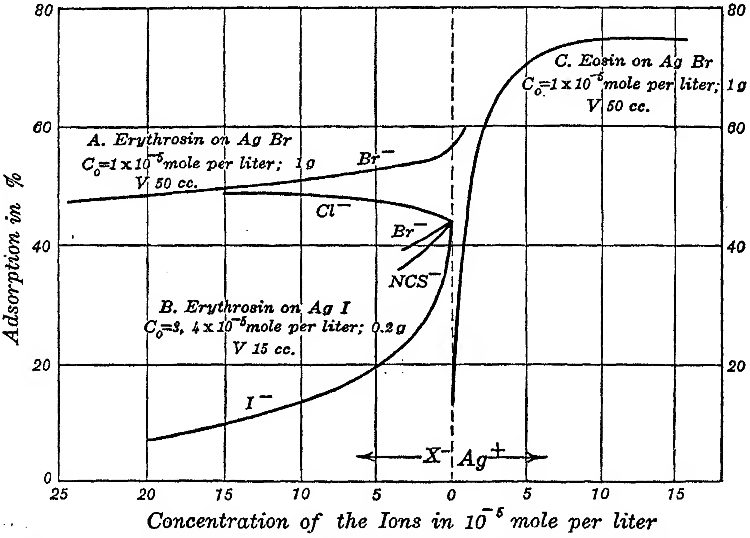

FIG. 4 Effect of anions (X^-) and of Ag^+ ions on the adsorption of erythrosin on AgBr and AgI and of eosin on AgBr.

If a solution contains both an electrolyte and a dye, the adsorption of the dye ion will be affected in a characteristic way if the adsorbent in question takes up predominantly the anion or the cation of the electrolyte. The case in which the more highly adsorbed ion of the electrolyte has the same sign as the dyestuff ion will be discussed first (the reverse case is discussed on page 222); it is immaterial whether they are both cations or anions.

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[29] In Figure 4 the ordinate values corresponding to abscissa *o* (this denotes that neither an excess of halide nor of silver ions has been added to the solution) of 5% in the Curve C for eosin, or of 55% in Curve A for erythrosin, refer to the same quantity of a certain silver bromide powder and to the same initial concentration of dyestuff.

In the case of the anions, the dye anion will compete with the anion of the electrolyte for the surface and the adsorption of *each* of the anions will depend both on the adsorbability and on the concentration of both. The adsorption of a particular dye anion will be encroached upon by the electrolyte to a greater extent the higher the concentration (more accurately, the activity) of the competing anion and the greater the latter's adsorbability. This makes it possible to compare the adsorbability of different anions on the basis of their ability to displace a dye anion. Obviously the same is true if a dye cation is displaced by various cations.

The Curves B in Figure 4 will serve as examples. They show how erythrosin, which under the given conditions, is adsorbed from a pure water solution to the extent of 43.5% by silver iodide, is displaced increasingly from the surface by rising concentrations of KBr, KSCN and KI. From the order of the displacing action, it can be deduced, according to the above, that the adsorbability on silver iodide increases[30] in the sequence

$$Cl^- < Br^- < SCN^- < I^-$$

For the three analogous halide ions this is, however, also the order of the decreasing solubility of their silver salts, which again is in conformity with the rule given above. However, for the strict validity of the rule the analogy of the ions must be quite extensive. This is shown by the case of the thiocyanate ion which is adsorbed better on silver iodide than is the bromide ion, even though the solubility of AgSCN (8×10^{-7} mole per liter) is somewhat greater than that of AgBr (5×10^{-7} mole per liter).

Furthermore, the adsorption of erythrosin on silver iodide is not lowered by adding potassium chloride, but is raised slightly.[31] That chloride ion is also adsorbed on silver iodide can be seen from Figure 5, which shows clearly the displacement of eosin by chloride ion. This diagram also indicates that iodide ion is adsorbed much better on silver iodide than is chloride ion (compare also Section 8).[32]

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[30] Compare the following regarding Cl^-.

[31] Intensive studies (11, 12) involving numerous electrolytes have shown that this is probably due to the predominance of a second effect that can be regarded as an increase of the activity of the high molecular dyestuff, a kind of salting out effect. Thus, there are also cases like that of the effect of potassium carbonate (12) on the adsorption of erythrosin on silver iodide, where with rising concentration of the electrolyte, there is first a lowering, then an increase in the adsorption of the dyestuff. Compare also Figure 12.

[32] The two curves of Figure 5 naturally will come together at the concentration $c = o$ of the halide ions (equivalent body of silver iodide), that in the logarithmic form lies at $-\infty$. The adsorbed portion there is 60%.

Further conclusions (important to the titration method) that can be drawn from the foregoing displacement experiments will be presented, but before taking up this matter two other questions will be discussed.

The Surface Development of the Adsorbents Active in the Titration and the Quantities of Indicator to be Employed. The surface exposure of the adsorbent is of great significance to the adsorption phenomena underlying the new titration method.

The surface development at the equivalence point, at which (or shortly before or after) the sol coagulates in many titrations, lies between that of the sol itself and that of the fine crystalline powders used in most of the adsorption experiments discussed here; actually the *surface development is closer to that of the sol.* The measurements by Dehio (8) and Walker (10) showed that in the adsorption of eosin up to saturation of the surface of a silver bromide powder or sol, the relation of the number of adsorbed dyestuff molecules to the total number of AgBr molecules of the powder or sol is

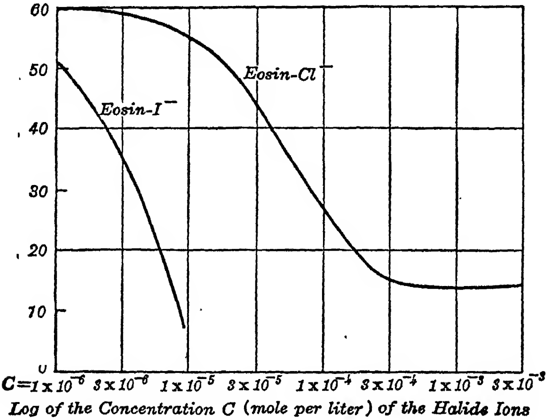

FIG. 5 Effect of KCl and KI on the adsorption of eosin ($C_0 = 2 \times 10^{-6}$ M/L) on AgI (0.1 g.) V = 20 cc.

$$8 \times 10^{-5} \text{ or} > 5 \times 10^{-3} \text{ mole dyestuff/mole AgBr.}$$

The latter figure (5×10^{-3}) sets *an upper limit* for the relative quantity of dyestuff that can be taken up in saturating the surface of the adsorbent produced in the titration. However, the total quantity of dyestuff added should be kept below this limit, because a distinct color change requires that a considerable fraction of the available dyestuff be adsorbed and in general, this is not the case near the saturation concentration (compare Figure 2).

In determining a lower limit for the quantity of dyestuff to be used, it is important to note that the light scattered by the sol or the suspension often influences the color intensity of the titration system quite adversely.

In practice it has been found that for titrations the optimum relative proportion in the various cases[33] lies between 2×10^{-4} and 3×10^{-3} mole dyestuff per mole silver halide, that is, in a range lying between the estimated values just given.[34]

Some latitude is available in any particular case, since with increased concentration of the dyestuff, within certain limits, there goes an increased protective action on the sol. This results in an extension of the adsorbing surface. When Fajans and Wolff (3) in certain cases, specified more dyestuff than Kolthoff (25) the reason was, in part, that they were trying to keep as much of the silver halide as possible in the sol form at the transition point. (Compare case 1, p. 234.)

A rounded off average value of 10^{-3} was taken for the above characteristic ratio of moles dyestuff/mole silver halide in the following approximate calculations.

General Consideration of the Course of Titration Curves with Adsorption Indicators. In view of the foregoing the following condition must be fulfilled if the titration of halide with silver salt and an anion indicator is to be made with an accuracy of 0.1%. A change in the composition of a solution from an excess of 0.1% of halide to a similar excess of silver salt requires that, of a quantity of dyestuff amounting to about 0.1% of the total silver halide, a part large enough to bring about a distinct color change must be transferred from the dissolved into the adsorbed state. Two extreme cases can be conceived; these are illustrated in Figure 6 A.

1. The adsorption on the equivalent body is small (in Curve a, = 0). Under this condition the excess of 0.1% silver ion must cause a considerable part of the dyestuff to be taken up.[35]

2. The adsorption on the equivalent body is considerable (in Curve b, 100%). In this case the dyestuff, whose molar quantity, as stated on

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[33] Compare (3), also (50).

[34] Dimethyl (R) diiodo (R) fluorescein, for which in the iodide titration the relation was 8×10^{-3}, is an exception [compare (3), p. 232].

[35] This case differs from one in which the indicator is precipitated by an excess of the precipitant, as in the Mohr titration, because here the indicator is removed from the solution before the solubility product concerned has been exceeded.

page 215, is between 0.02 and 0.3% of the molar quantity of the precipitate, must be displaced to a large extent from the surface by 0.1%, that is by, at most, the five fold quantity of excess halide ions.

Between these extremes there are intermediate cases in which the transition interval lies between an excess ($\leqslant 0.1\%$) of halide ions and a similar excess of silver ions. Figure 6B shows an example which lies in the middle between the limiting cases a and b of Figure 6A. The form of the curve is completely analogous to the titration curves of neutralization or precipitation analyses.[36]

Before showing, in the next Sections, the extent to which the behavior of some adsorption indicators conforms to the idealized curves of Figure 6, several general viewpoints will be discussed on the basis of the results recently obtained with Van Artsdalen (16). These studies dealt with the adsorption of the acid dye chromotrope F4B on silver iodide powder.[37] This dye was recommended by Belladen and Piazza (27) for the titration of bromide and iodide as well as of iodide in the presence of chloride (compare p. 224).

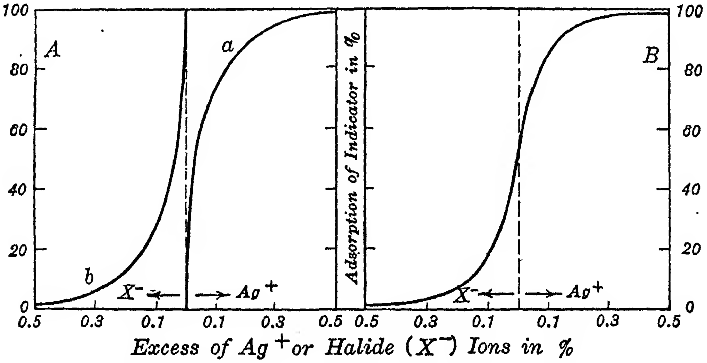

FIG. 6 Idealized adsorption or titration curves.

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[36] Compare Kolthoff (25), Part I.

[37] This dyestuff, the sodium salt of a sulfonic acid ($C_{20}H_{12}N_2O_7S_2Na_2$) is not one of the best indicators for practical use because its color changes show little contrast. It has proved more suitable, however, for a closer study of adsorption curves than the derivatives of fluorescein used at first, because in the absence of the adsorbent it remains in solution even in the presence of a considerable excess of silver ion. The absorption spectrum of a solution of the dye (1×10^{-5} mole per liter) is not changed by the presence of silver nitrate (5×10^{-4} mole per liter). Compare, in contrast, the behavior of erythrosin as shown in Figure 9, Curve s. With methyl violet, studied first by Hodakow (37) complications arose at higher concentrations of the dye.

A comparison of Curves I and II in Figure 7 reveals how strongly the *steepness of the curves,* which indicate the effect of the excess Ag^+ or I^- on the *percentage*[38] of the dyestuff adsorbed[39] depends, for a given titration system (adsorbent-dyestuff), on the *quantity of dyestuff.*[40] Under like conditions, for both curves, the relative quantities are about 1:20.

Now it is easy to understand that the steepness of the *influence curve* of a given titration system depends primarily in what portion of the adsorption isotherm (compare Figure 2) the point on the influence curve corresponding to the equivalent body falls. In curve II of Figure 7, this point (13.3% adsorption corresponding to 2.65×10^{-7} mole/1 g. AgI) is identical with point 5 of Figure 2; the adsorbed quantity amounts to 83% of the saturation value (3.18×10^{-7} mole/1 g. AgI). On the other hand, the corresponding point of curve I (54% or 5.6×10^{-8} mole/1 g. AgI) is identical with point 1 of Figure 2; in this case only 18% of the total available surface of the equivalent body is covered with dyestuff.

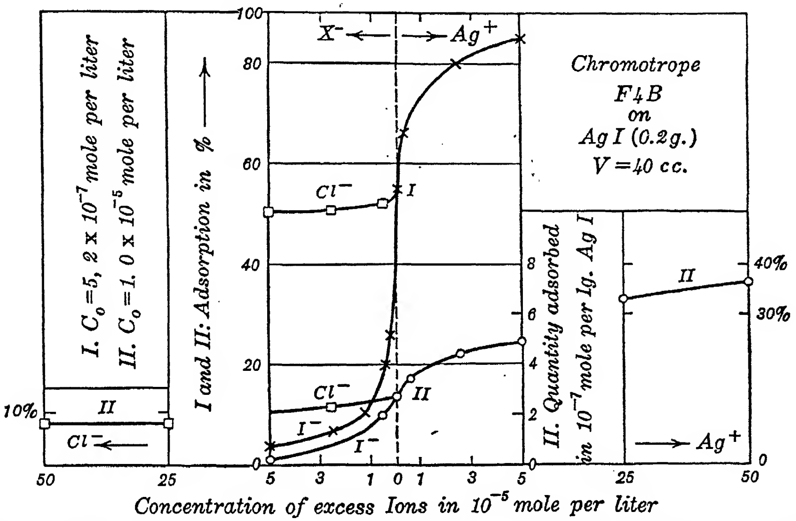

FIG. 7 Effect of Ag^+, I^- and Cl^- on the adsorption of chromotrope F4B at two initial concentrations C_0 of the dye.

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[38] The analogous comparison of the effect on the *absolute* quantities adsorbed is of no interest in evaluating the titration.

[39] Compare p. 226 as to the branches marked Cl^-.

[40] In the first studies of this topic by Wolff (3) and Hodakow (37) the surface development was insufficiently defined for an exact comparison.

When, at a given concentration of dyestuff, the surface of the equivalent body is almost saturated, no further increase of adsorption would be expected to follow the addition of an excess of the oppositely charged ions. In the adsorption of erythrosin on silver bromide (10) and also of wool violet 4 B N on lead sulfate (21) the same saturation value is reached in the presence of an excess of Ag^+ or of Pb^{++} as for the corresponding equivalent body, even though for the latter, only at a higher dyestuff concentration. However, chromotrope F4B behaves differently. The right half of Figure 7 shows that even at a concentration of Ag^+ of only 5×10^{-5} mole per liter, the quantity adsorbed reaches a value (4.9×10^{-7} mole/1 g. AgI) which clearly exceeds the saturation values on the equivalent body (3.18×10^{-7}). The curve continues to rise distinctly at still higher concentrations of silver ion and at 50×10^{-5} mole per liter, 7.2×10^{-7} mole/1 g. AgI is adsorbed, that is, more than twice as much as corresponds to the saturation value on the equivalent body.

This finding is of great interest in elucidating the mechanism of these adsorption phenomena. Thus Kolthoff (21–24) interprets the fundamental phenomenon in the adsorption of a dye anion as an exchange with the anions of the lattice surface of the adsorbent. The rôle of an excess of cations then consists merely in diminishing the concentration in the *solution* of the anions of the lattice itself. These anions are competing with the dye anion for the surface. It might be expected then that, in general, the saturation value in the presence of an excess of cations (in the adsorption of a dye anion) would be the same as on the equivalent body.[41] The *contrary behavior* of the system chromotrope F4B — AgI, however, shows that the surface of a silver body, in the sense of Figure 1a, actually can possess more active centers for the adsorption of anions than that of an equivalent body.

Even though, in Curve II, in the region of excess silver ions, the quantity adsorbed rises to more than double the value on the equivalent body it still can furnish no usable titration curve. The percentage adsorption of the dyestuff near the saturation point on the equivalent body, in general, is small and so the approximately equal total, gradual increase of the adsorption is also small.

The conditions represented in Curve I are different. Here the considerable adsorption of 54% of the total quantity of dye amounts to only 18% of the saturation value of the surface of the equivalent body. Under these circumstances, through the effect of the action of the silver body, considerable additional portions of the dyestuff can be taken up. This explains why the addition of 0.5×10^{-5} mole per liter of silver ion causes the adsorbed portion in Curve I to rise from 54% to 70.5%, in Curve II from 13.3% to 17.5%, that is, 15.5% in contrast to only 4.2%, figured on the basis of the total quantity of dyestuff.

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[41] As mentioned above, this is the case in the systems erythrosin—AgBr, and wool violet—$PbSO_4$. It will be interesting to determine whether it is more than mere chance that these systems are not suitable for the titration.

The difference in the slopes of those parts of Curves I and II lying in the region of excess iodide ion, that is, the *steepness of the displacement curves* of the two different quantities of dyestuff will now be emphasized numerically. By the addition of 0.5×10^{-5} mole per liter of excess iodide ion. the portion adsorbed on the equivalent body is diminished for Curve I from 54% to 20.5%, that is, by 33.5%, for Curve II from 13.3% to 9.6%, that is, by only 3.7% of the total quantity of dyestuff present. From this comparison of the steepness of the branches of Curves I and II below the equivalence point, it is quite plain that I is much more favorable for the titration than II.

It is interesting to compare the quantities of dyestuffs, referred to the quantity of adsorbent, used in the adsorption measurements of Figure 7 with those used in actual titrations. From the statements of Belladen and Piazza (27), the molar ratio dyestuff/silver iodide is about 7×10^{-4}.[42] From the data of Figure 7, the ratio in question for Curve I is calculated to be 2.35×10^{-5}, for Curve II, 4.7×10^{-4}. Therefore, in the titration, this ratio is still somewhat greater than that of the less favorable Curve II. However, the surface development of the silver iodide produced during the titration is considerably greater than that of the powder used in the adsorption experiments (compare p. 214), so that the degree of saturation of the surface on the equivalent body is certainly smaller in the titration than in Curve II. But since, in a usable titration the influence curve must be steeper than curve II, it may be concluded that, for a given titration system, the steepness of the influence curve actually is dependent on the degree of saturation of the surface of the equivalent body.

If the steepness of the influence curves of different titration systems are to be compared, they must refer to a *like degree of saturation of the surface* of the equivalent body. This holds also for other quantities, for example, that used (following the suggestion of the writer) as a rough measure of the steepness of the displacement curves, the *relative half-value*

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[42] The results of the titration, with a constant quantity of dyestuff (3 drops of 0.5% solution), are independent of how much water, within the limits of 50-400 cc., was used for diluting the 20 cc. of 0.1 N potassium iodide solution. Consequently, in the titration the relative quantities of dyestuff and sol are the principal factors, not their absolute concentrations.

concentration, H_r. By this is meant that ratio of the total molar concentrations of halide ion and dyestuff at which half of the dye taken up on the equivalent body is displaced. H_r may be expected to rise as the degree of saturation decreases. This is confirmed in Figure 7. In Curve II, at a total concentration of the dyestuff $c_0 = 1 \times 10^{-5}$ mole per liter, a lowering of the adsorption from 13.3% to 6.7% required the addition of 1×10^{-5} mole per liter of iodide ion. Therefore, $H_r = 1$. However, in Curve I, $c_0 = 5.2 \times 10^{-7}$, a decrease of the adsorption from 54% to 27% requires 2.5×10^{-6} mole per liter of iodide ion; consequently $H_r = 4.8$.

In the system chromotrope F4B + AgI, which is suitable for titration purposes, the relative half value concentration H_r is equal to unity in the neighborhood of the saturation of the surface of the equivalent body, and even when the concentration of the dye is twenty times less the value of H_r does not exceed 5. It may be expected that in systems, which even in the vicinity of saturation show considerably higher values of H_r, the displacement curve is too flat to make a usable titration possible.

Several Examples of the Displacement of Dyestuff Ions by Ions of Like Sign. Pursuant to the general viewpoints set forth in Section 5, the very instructive behavior of erythrosin will be discussed in detail. From Curve A [Walker (10)] in Figure 4 it can be shown easily that the system, *AgBr — erythrosin — Br^-* by no means conforms to the conditions stated in 2 on page 215. At a total concentration of erythrosin of 1×10^{-5} mole per liter, the small reduction of the adsorption from 55%, at which the surface was almost saturated, to 51% or to 47.3%, requires the addition of 1×10^{-4} or 2.5×10^{-4} mole per liter of bromide, a multiple of the dyestuff concentration. In this case, $H_r \gg 25$. Accordingly, when titrating bromide in the presence of erythrosin a decided color change occurs long before the equivalence point is reached.

It was shown for all silver halides as adsorbents that the adsorbability of the chloride ion is still farther below that of erythrosin. Obviously, *erythrosin is no more applicable to the titration of chloride than of bromide.*

The displacement curve I^- of Figure 4 B in the system *AgI — erythrosin* will be discussed next. In this case also, the surface of the equivalent body of the silver iodide powder was almost saturated, and from the curve it appears that $H_r = 1$, the same value as for Curve II of Figure 7 for chromotrope F4B. In spite of this, at the greater development of surface that exists in a titration system, the behavior of erythrosin is not entirely like that of chromotrope. Fajans and Hassel (1) pointed out that the color change with erythrosin is not sharp when considerable quantities of silver iodide are present. According to Fajans and Wolff [(3) p. 242] erythrosin is also unsuitable in the exact determination of iodide.

Direct experiments of Pruckner (13) showed that when 200 cc. of 0.01 N potassium iodide was titrated with 0.1 N silver nitrate in the presence of 5×10^{-6} mole per liter of erythrosin, a distinct transition interval was obtained, to be sure, but its beginning or end, however, was about 1.2% or 0.1% [43] before the equivalence point as determined with eosin. That means, however, that the adsorption is complete even in the region of excess iodide ion (Curve B in Figure 6).

An extensive study by Rudenko (50) of the effect of foreign salts on the titrations with adsorption indicators showed that iodide can be determined very accurately with erythrosin in the presence of nitrates, sulfates and acetates of various uni- and bivalent metals. This was checked for manganous sulfate by Pruckner. Under the conditions given above, but in the presence of twenty times the equivalent (with respect to potassium iodide) quantity of manganous sulfate as recommended by Rudenko, the value agreed within 0.1% with that obtained in the eosin titration.

Rudenko rightly connected this effect of foreign salts with their coagulating action on silver iodide. The diminution of the surface represses the adsorption of the dye on the equivalent body and this may so affect the position of the transition interval that the titration curve of the Form b in Figure 6 may go over into Curve B or even into a.

While erythrosin, because of its great adsorbability, is suitable only for the titration of iodide, and even then only under special conditions, the utility of the less adsorbable eosin (compare page 210) is much greater. Only toward *chloride ion*, the most weakly adsorbed of all, does eosin behave as erythrosin does toward bromide ion, and it cannot be used for the determination of chloride ion.[44]

Eosin is only slightly adsorbed on the equivalent body of silver bromide (compare Figure 4, C). In order to study the displacing action of bromide ion at all, there had to be used in the experiments by Wolff (3) (with a dye concentration of 6×10^{-5} mole per liter) a sol of high dispersity (about 3×10^{16} particles per mole) or silver bromide powder (0.1 g.) which Schneller used at the very low dyestuff concentration, 1×10^{-6} mole per liter, in which case 26% of the eosin was adsorbed on the equivalent body. Wolff found H_r to be about 2, while Schneller's figure, probably because of less dense surface coverage, was about 5.

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[43] These figures are averages of rather divergent values.

[44] Compare (1). According to Weir (9) $H_r \sim 10$ in the system AgCl-eosin-Cl^-.

It follows that the *displacement curve of the system* $AgBr - eosin - Br^-$ is not more favorable than that of AgI − erythrosin − I^-, where $H_r =$ approximately 1. If nevertheless eosin is excellent for the determination of bromide, the reason must be that the adsorption is only slight on the equivalent body and even smaller in the range of excess bromide ions, and the titration curve approaches case a in Figure 6 A. This is discussed in the following Section.

The Effect of an Excess of an Oppositely Charged Ion on the Adsorption of the Indicator. Figure 4 C (10) shows that the sharp increase in the quantity of eosin adsorbed on silver bromide powder brought about by a slight excess of silver ion corresponds closely to the requirement of the extreme case 1, page 215. Under the conditions given in Figure 4 C the adsorption at the equivalence point is actually slight (5%). In contrast, at a total concentration of excess silver ion of only 2×10^{-5} mole per liter, equivalent to an addition to the total volume of 50 cc. of 1×10^{-6} mole silver nitrate (for instance 0.05 cc. of 0.02 *N* solution) 56% of the dyestuff is adsorbed. This causes a distinct color change.[45] In this case, the quantity of pulverulent adsorbent was 1 gram, about 5×10^{-3} mole; the excess of silver ion, 1×10^{-6} mole, amounts therefore to only 0.02% of the total quantity.

Therefore, while approximately 1×10^{-6} mole of excess silver nitrate can be expected to cause a change, the whole transition interval will be considerably greater because a flat portion corresponding to a further gradual taking up of eosin joins on to the steep part of the curve. In this curve, which presents measurements made with 1 gram of silver bromide powder, saturation of the surface is reached with about 1×10^{-4} mole per liter, corresponding to 5×10^{-6} mole of silver nitrate; about 74% of the dye is adsorbed. In a practical titration (2.5×10^{-3} mole bromide) the separate conditions are different in some respects, but the whole titration curve could not have deviated markedly from Curve C of Figure 4. On one hand, the surface development in the titration is greater than in the adsorption measurements, despite the fact that the quantity of silver bromide is only half as great. On the other hand, in the adsorption measurements the molar ratio (10^{-4}) dyestuff/AgBr is smaller than in the titration ($\sim 10^{-3}$). Actually, in a titration of 0.02 *N* potassium bromide solution with 0.1 *N* silver nitrate, the interval in which a color change could be detected was 1×10^{-5} mole silver nitrate, which corresponds to 0.4% of the total quantity titrated.[46] If the titration is carried to the first distinct color change (for details see the Practical Part) the correct equivalence point can be reproduced within 0.1%.[47] Beyond this, the titration curve is only somewhat less steep than Curve C in Figure 4.

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[45] As will be shown on page 228, with erythrosin as example, only a part of the adsorbed dye has an absorption band different from that of the dissolved dye. If the data of Figure 10 could be transferred directly to eosin, at 56% adsorption about 40% of the total dye would exhibit the changed color.

Figure 4 C and the color change during the titration deal with an *adsorption* of eosin and not, say, with the precipitation of slightly soluble silver eosinate because its solubility product has been exceeded in the homogeneous aqueous solution.[48] This is proved by the following calculation: the solubility of silver eosinate is 5×10^{-5} mole per liter and its solubility product, therefore, is 125×10^{-15} (mole/liter).[3] The initial concentration of eosin in Figure 4 C was $c_0 = 1 \times 10^{-5}$ mole/liter, so that even with the total concentration of silver nitrate of 5×10^{-5}, at which already 70% of the eosin is removed from the solution, the ion product amounts to only 25×10^{-15} mole/liter.

Finally, reference is made again to the demonstration experiment (page 205) which indicates that in order to obtain a color change visible to the eye in an eosin solution (5×10^{-6} mole per liter) containing no silver bromide, silver nitrate must be added until its concentration is much greater than is necessary to produce the color change in a titration. For details see p. 205, footnote 13 and also (7).

Determination of Iodide in the Presence of Chloride. Adsorption indicators make possible the direct argentometric determination of iodide in the presence of chloride. In the first experiment along this line by Fajans and Hassel (1) eosin was used as indicator because it had been shown qualitatively that this dye is readily displaced from the surface of a silver halide by an excess of iodide ion, but only incompletely displaced by chloride ion. Hence, in the titration with Ag^+, when all the iodide, which forms the less soluble silver salt, has reacted, adsorption of eosin and the consequent color change could be expected even when chloride is present. It was found however, that at the molar ratio $KCl:KI = 1:1$ the color change did not appear exactly at the point when silver equivalent to the iodide had been introduced, but only when this point had been passed by about 1%. This was explained as due to some chloride being carried along with the silver iodide. Fajans and Wolff (3) have shown that similar results are obtained with dimethyl(R)-diiodo(R) fluorescein, diiodo(R) fluorescein and rose Bengal. The over-consumption of silver nitrate was found to depend on the ratio $x = KCl:KI$. For instance, with the first indicator, this excess consumption rose to a very flat maximum of 1% for values of x between $0.1 - 0.5$; with larger quantities of potassium chloride it fell off; when $x = 4$, the over-consumption was 0.45%.

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[46] This interval (here and in analogous cases) can be determined quite simply if near the equivalence point the colloidal solution or fine suspension is divided between two beakers. The next drop of silver nitrate is added to one of the beakers. If a change occurs the contents of both beakers are mixed together. This procedure is continued until a change can no longer be detected. The interval can be traversed in the reverse direction if potassium bromide is added.

[47] So far as is known now the behavior of eosin in the bromide titration corresponds to a titration curve lying between Curve C in Figure 4, which is of the type of Curve a in Figure 6, and Curve B in Figure 6. Compare page 244. Further studies may make possible a more definite statement on this matter.

[48] These phenomena may be explained also on the basis that the solubility product of silver eosinate is smaller at the interface: aqueous solution—AgBr, than in the homogeneous solution. This is the case for example for the interface: aqueous solution—benzene, etc., as shown by the experiments of Deutsch, Zeit. physik. Chem. *136*, 363 (1928).

Kolthoff (18) found that even this small over-consumption can be avoided by adding ammonium carbonate, and then the change occurs with a quantity of silver equivalent to the iodide.

The excess consumption when iodide is titrated with silver nitrate in the presence of chloride can be decreased also by the procedure used by Berry.[49] The titration is started with 0.1 N solutions and before the equivalence point is reached the precipitated silver iodide is coagulated by the addition of lanthanum nitrate. Then the titration is continued with 0.01 N silver nitrate in the presence of rose Bengal until the color of the supernatant solution is discharged. With a ratio $KCl:KI = 1:3$, the over-consumption was only 0.3% as compared with 1.2% found by Fajans and Wolff.

Belladen and Piazza (27) have made an interesting discovery with the acid dyes brilliant archil C and chromotrope F4B, which they recommend as adsorption indicators. These are suitable for the silver titration of all three halide ions, that is, the dye anions can be displaced from the surface of silver chloride by an excess of even chloride ion. Nevertheless when a mixture of iodide and chloride is titrated, a color change is obtained as soon as the quantity of silver ion approximately corresponds to that of the iodide alone.

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[49] Private communication supplementing (30).

Belladen and Piazza state that up to a ratio of $x = \mathrm{Cl}:\mathrm{I}$ of about 1, the latter volume is exactly equivalent to the iodide, and that only at higher values of x can a smaller over-consumption of silver ion be found. The writer found an over-consumption of several parts per thousand with both indicators even when $x = 0.5$. The addition of ammonium carbonate does not make it possible to obtain a more distinct color change when brilliant archil or chromotrope is used.

No suitable adsorption indicator has been found, as yet, for the titration of iodide in the presence of bromide, or of bromide in the presence of chloride.

The facts given above are explained by Figure 5 which exhibits the adsorption of eosin on silver iodide as measured by Pruckner (13). Since bromide can be determined with the aid of eosin (compare page 222) it is evident that it is also suitable when iodide is titrated alone. The displacement curve in the system AgI — eosin — I^-, as may be seen, is quite steep, iodide ion at a concentration of 1×10^{-5} mole per liter almost completely displaces the eosin, whose molar concentration is one-fifth as great.

Although eosin is displaced much less strongly from the AgI surface by chloride ion, a concentration of 3×10^{-4} mole per liter suffices to reduce the quantity (60%) adsorbed on the equivalent body to about one-fourth (14%). Fajans and Hassel (1) and Kolthoff (18) have succeeded in titrating iodide with eosin in the presence of a chloride concentration of 4×10^{-3} mole per liter or even as much as 0.3 mole per liter. If the curve: eosin — Cl^- in Figure 5 had the same slope for higher concentrations that it has in the range of chloride concentrations between 3×10^{-5} and 3×10^{-4} mole per liter then, even for about 3×10^{-3} mole per liter of chloride ion the adsorption of eosin would become imperceptibly small, and a color change, after the iodide had reacted, would be impossible.

It is very remarkable that the curve becomes much less steep at concentrations of chloride ion above 3×10^{-4} mole per liter.[50] In Pruckner's measurements, the adsorbed quantity up to a concentration of 4×10^{-3} mole per liter (beyond the limits of Figure 5) remained constant (14%) within the error of the experiment. However, a qualitative test on a silver iodide sol showed that the addition of increasing quantities of a concentrated potassium chloride solution[51] causes the continual displacement of more eosin, but even at a concentration of 0.3 mole of KCl per liter (coagulation occurs here) a considerable quantity still remains adsorbed.

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[50] The theoretical interpretation of this very slowly descending portion of the displacement curve, as will be only indicated here, is certainly to be found in the idea (recently supported by several facts) that various portions of the surface differ materially with respect to their adsorption potentials.

These experiments explain the observation in the eosin titration of iodide in the presence of chloride; when large quantities of chloride are added, the adsorbed quantity patently falls in the flatly descending portion of the adsorption curve. It is easy to see that the sharpness of the change will be decreased by considerable quantities of chloride [compare (3) p. 231], since after the iodide has reacted only a part (in Figure 5 only 14%) of the dyestuff will be adsorbed.

In the case of adsorption of chromotrope F4B on silver iodide, the displacing action of chloride ion is slight, as may be seen in Figure 7 for both dyestuff concentrations. In Curve II the portion (13.3%) adsorbed on the equivalent body gradually decreases to 8% as the quantities of chloride ion rise to a concentration of 5×10^{-4} mole per liter, whereas the dyestuff is displaced almost completely by 5×10^{-5} mole of iodide per liter.

The fact that iodide in the presence of 0.01 *N* chloride ion, for instance, can be titrated with various anionic indicators may be considered from still another point of view. Since the solubility product of silver chloride is 10^{-10}, in a solution like the one under consideration the concentration of silver ion is only 10^{-8} mole per liter. It can be concluded then that the color change, and therefore also a perceptible adsorption of the dye anions on the silver iodide will occur, even at the low concentration of silver ion present in the saturated solution of silver iodide in pure water (equivalent body).

The over-consumption of silver ion when titrating iodide in the presence of chloride can be ascribed to coprecipitation of silver chloride with the silver iodide. Portillo's (14) direct studies indicate this. The solubility of silver chloride in ammonium carbonate explains why this coprecipitation can be prevented by the addition of the latter material. However, as yet, there has been no explanation why a maximum over-consumption is observed for a particular ratio of KCl : KI.

The Color Change Accompanying Adsorption. The color changes occurring when a dyestuff is taken up in a polar adsorbent are the basis of these titrations. In the case of fluorescein and its derivatives these changes were connected by Fajans and Hassel (1) with the very widespread phenomenon of the alteration of optical properties (refraction, absorption and recently, Raman Effect) that ions undergo in the force fields of oppositely charged and neighboring ions. Since these changes must be due to some effect on the given electron system without in many cases any previous knowledge of the nature of the accompanying physical[52] or chemical[53] modifications of the ions, *deformation of the electron shells* was generally inferred, to avoid superfluous, hypothetical assumptions. Numerous regularities have been established which involve the dependence of the deformation phenomena on the properties of the participating ions. For the new titration method the most important fact is that particularly great changes of the electronic systems of the ions occur when heavy metal cations, silver ions for example, with no noble gas character unite with easily deformable anions such as halide or dyestuff ions. In fact, in such cases, the very pronounced deformation of the ions exhibits itself both in favoring the adsorption of excess ions on the slightly soluble precipitates and also in the very considerable color changes shown by the indicator at its adsorption.

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[51] The procedure given on p. 223, footnote 46, proved useful in this case: before adding a further quantity of potassium chloride solution, the sol was divided.

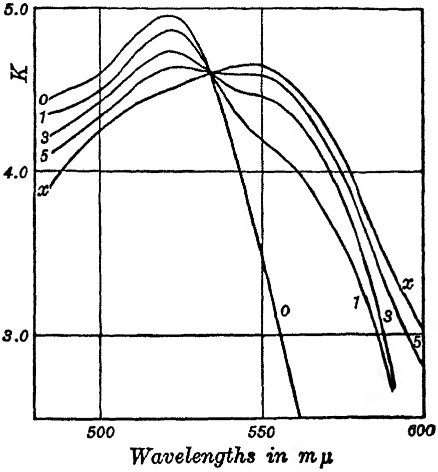

FIG. 8 Light adsorption in the system: sodium erythrosinate ($C_0 = 5 \times 10^{-6}$ mole/liter for all curves) + AgI sol (10^{-4} mole/liter for curves 1, 3, 5, *x*, zero for curve 0). + $AgNO_3$ (1, 3, 5 gives the corresponding C_0 in 10^{-6} mole/liter); *x* is the curve of the erythrosin completely adsorbed on AgI, see text.

A closer insight into the nature of this color change is given by studies of the *light absorption* of several dyestuffs adsorbed, under various conditions, on colloidal silver iodide. Schneller (11) made the first experiments along this line with phloxin and rhodamine 6 G, and the writer and Farnsworth (15) studied erythrosin, which is particularly suited to this purpose. Our results put the earlier conclusions on a broader experimental basis.

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[52] Change of the energy of ionization, or of the transition probability of electrons, or else polarization of the electronic shells in the electro-static fields of the adjacent ions.

[53] Production of new homopolar bonds, or shifting of atoms and linkages within the molecule.

In Figures 8 and 9, *o* is the absorption curve[54] of a very dilute water solution of sodium erythrosinate alone. The other curves refer to the same total concentration c_0 of the dye and (with the exception of Curve *s* in Figure 9) in the presence of 10^{-4} mole/liter of a silver iodide sol. Excess potassium iodide (for the Curve I^-) or silver nitrate (for the other curves) was added to the solution to stabilize the sol and at the same time influence the adsorption of the dye. Figure 10 gives a general survey of all the experiments.

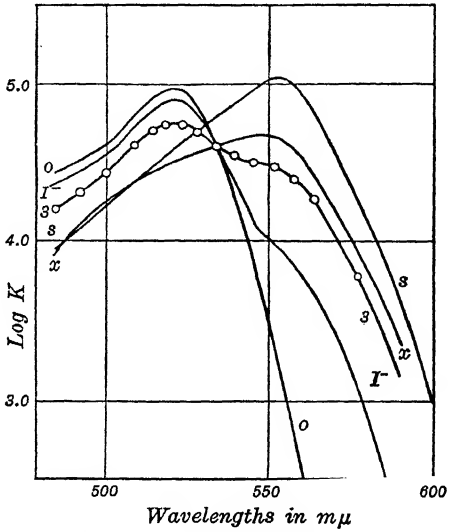

FIG. 9 Light adsorption of sodium erythrosinate, 5×10^{-6} mole/liter under various conditions. Curves *o*, *3* and *x* compare Fig. 8. In curve *3*, *o* are the experimentally determined points, the resulting curve is made up of 40% of curve *o* and 60% of curve *x*. Curve I^-: erythrosin adsorbed on AgI sol (10^{-4} mole/liter) in presence of 0.5×10^{-6} mole/liter of KI. Curve *s*: erythrosin + 10^{-4} mole/liter of $AgNO_3$ (without AgI).

As may be seen, parallel to the increasing adsorption (compare the Curves *a* in Figure 10) in the series I^-, *1*, *3*, *5*, the absorption maximum of the dissolved dye anion at 521 mμ is lowered in increasing measure and the absorption broadened steadily toward longer wave lengths, with the appearance of a new flat maximum at 547 mμ. This is completely developed in Curve *x*, the maximum 521 mμ can no longer be discerned. The measurements showed that the form of the absorption curve does not change appreciably if the concentration of excess Ag^+ is progressively increased from 0.1×10^{-4} mole/liter (abscissa 2.0 in Figure 10) at which the erythrosin already is practically 100% adsorbed on the silver iodide sol, up to 1×10^{-4} mole/liter). Curve *x* can therefore be taken as the *absorption band* of the erythrosin *completely adsorbed* on silver iodide.

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[54] The relation of the logarithm of the decadic molar extinction coefficient *k* [in cm^{-1} $(mole/liter)^{-1}$] to the wave length.

Closer study of these interesting findings reveals that the absorption curves obtained either with excess iodide ion or with excess silver

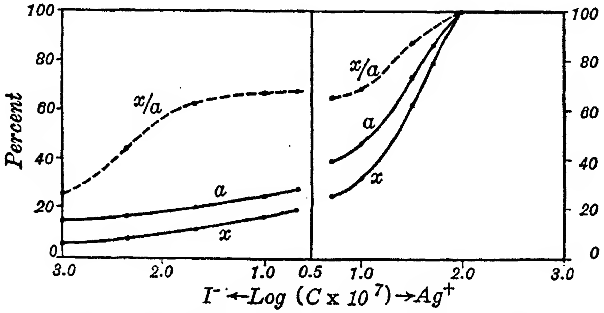

FIG. 10 Influence of the concentration of the excess $AgNO_3$ or KI (in presence of 10^{-4} mole/liter AgI sol) on the percentage of erythrosin adsorbed (curves *a*) or showing the band *x* of Fig. 8 ($C_0 = 5 \times 10^{-6}$ mole/liter). Curves *x/a* therefore represent the percentage of the adsorbed dye exhibiting the band *x*.

ion can be represented as the sum[55] of the two absorption bands 0 and *x* for the dissolved and for the completely adsorbed anion respectively.[56] However, the fraction (*x* in Figure 10) of dyestuff ions, to which the band *x* refers, is not, as might naturally be assumed, identical with the fraction *a* of the ions adsorbed as determined by ultra-filtration.[57] On the contrary, the quantity *x/a* increases with falling concentration of iodide ion and rising concentration of silver ion in the solution. Thus the band *x* is shown by only 25% and 65% respectively of all adsorbed dyestuff ions at excess iodide ion of 10^{-4} and 5×10^{-7} mole/liter (abscissae 3.0 and 0.69 in Figure 10). With excess silver ion, *x/a* continues to increase and at a concentration of about 10^{-5} mole/liter of silver ion—the dyestuff is practically completely adsorbed here—the whole dye absorbs in band x.

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[55] The clearest evidence that the dye, in the optical sense, is in the condition corresponding to *either one* or *the other* of the bands, is that all the curves of Figures 8 and 9 (except Curve *s*) cut each other *at one point*, at the wave length 535 mμ. The extinction constant for the two bands *0* and *x* are equal here, and therefore the total absorption is independent of the proportion of the two states.

[56] Compare the explanation of Curve 3 below Figure 9.

[57] de Boer and Custers, Zeit. physik. Chem. (B) *21*, 208 (1933); *25*, 238 (1934) in their study of the light absorption of gaseous iodine and *p*-nitrophenol molecules adsorbed on calcium fluoride, obtained results analogous in many respects to those

The natural assumption that the alteration of the chromophore on adsorption is caused by close contact of the dehydrated erythrosin anion with the dehydrated silver ions is supported by the following fact. In Figure 9, s represents the absorption curve of a system in which the erythrosin is almost completely precipitated as colloidal silver erythrosinate. This was accomplished by the addition of silver nitrate (1×10^{-4} mole/liter) ; no silver iodide was present. As may be seen, the maximum of Curve x of the erythrosin anion completely adsorbed on silver iodide (547 mμ) lies very close to the maximum of the anion built into the lattice of its silver salt (552 mμ).[58] These findings argue for the view that the change of color occurs only when the chromophore of the dyestuff has a suitable orientation with respect to the silver ions on the surface. The contact not only with excess adsorbed silver ions but also with the silver ions of the lattice surface itself is effective here, because the band x, as already stated, is found in part with such erythrosin anions as are adsorbed on the *halide body* of silver iodide.

Since this contact of silver and dyestuff ions results in the appearance of a new characteristic absorption band, it may be that a new homopolar bond is formed by this deformation of the electron shells of the participating ions.

A more extended investigation of these relationships would also be of interest with regard to the various types of adsorption—addition adsorption or exchange adsorption—compare p. 208.

Theory of the Basic Adsorption Indicators and the Special Behavior of Phenosafranin as Indicator in Argentometric Titration. The theoretical bases of the action of adsorption indicators as developed in the preceding Sections were discussed from the standpoint of acid dyes. The discussion of the behavior of basic dyes will be limited here to the following points.

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[58] Even though the proximity of the two maxima indicates that the changes undergone by the dyestuff anion on adsorption and when precipitated as silver salt are analogous, these very absorption measurements show clearly that the first case cannot be merely the formation of silver erythrosinate on the surface of silver iodide. The Curves x and s in Figure 9, which result at an initial concentration of silver nitrate of 10^{-4} mole/liter, with or without silver iodide, are not identical, nor is it possible to form Curve x from a portion of Curve s and another band. It may be mentioned also that at an initial concentration of silver nitrate of 5×10^{-6} mole/liter, 70% of the erythrosin is adsorbed in the presence of silver iodide and 60% shows the band x, whereas without silver iodide, only about 2% of the dye absorbs in the band s, that is, precipitates as silver salt, while 98% remains in solution.

Since the active constituent of a basic dye is the cation, obviously in applying the above considerations the sign will be reversed, that is, the adsorption of the indicator will be prejudiced by positively charging the adsorbent and favored when it is negatively charged. The adsorption of methyl violet on silver chloride precipitates [Hodakow (37)] and of phenosafranin on silver bromide powder [Fig. 11] according to Weir (9) and Ketterl (12) are examples.

The case of phenosafranin will be discussed in some detail; in some respects, its behavior is exceptional among the adsorption indicators that have been studied thoroughly.[59]

In the cases discussed previously, the adsorption indicators are characterized by the following properties:

1. A considerable increase in adsorption occurs on going, during the titration, from a small excess of the constituent of the precipitate whose charge is like that of the dyestuff ion to a slight excess of the oppositely charged constituent of the precipitate.

2. The color change is conditioned by the change of color of the dyestuff ion at its transition from the dissolved state to that state in which it is adsorbed in the presence of an excess of the oppositely changed ion. Obviously the same holds when the transition is in the reverse direction.

The first instance of the titration of bromide and silver nitrate with phenosafranin as indicator, discovered in 1926 by Weir and the writer (9),[60] cannot be referred back to these principles. For contrary to 1, a considerable excess of bromide or silver ions is required to bring about a decided change of the adsorption of this basic dye. The slight slope of the curve in Figure 11 in comparison to other adsorption curves of usable indicators can be seen from the mere fact that in Figure 4 (compare Curve C and even Curve I^-) 10^{-5} mole/liter was used as the concentration unit of the excess ions, while in Figure 11, 10^{-4} mole/liter was chosen. Further, in opposition to 2, no material color change occurs at the adsorption of the dye cation in the region of excess bromide ions;

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[59] The peculiarities are not conditioned by the basic nature of phenosafranin, because rhodamine 6 G shows a behavior analogous to the acid dyes [compare (2)]. For example, the fact that in the presence of this dyestuff silver can be titrated very well with bromide, but not with iodide [(2), p. 241] is because the displacement curve in the system AgI—rhodamine 6 G.—Ag^+ is very flat (12).

[60] Berry and Durrant (28) unaware of Weir's dissertation, also pointed out the suitability of phenosafranin for this titration.

both solution and adsorbate are red. The change to blue takes place on passing the equivalence point from an excess of bromide to an excess of silver ion and it is therefore accompanied by a displacement, even though slight, of the dyestuff from the surface. One drop of 0.05 *N* solution is sufficient to cause a change from red to blue and vice versa. The change of color which, as special experiments have shown, is undergone only by the dyestuff adsorbed on the surface of the silver bromide, but not by that in the solution, obviously occurs when silver ions are taken up by the system AgBr − phenosafranin.

In addition to this necessary but not sufficient condition for the color change, is the further requirement that nitrate ions must be taken up at the same time, since the change to blue occurs only when the titration is made with silver nitrate, or if nitrate ions are present in the solution when titrating with silver perchlorate, etc.[61] Patently the blue color arises from a complex of phenosafranin and silver nitrate taken up on silver bromide. The special rôle of the combination of nitrate and silver ions may also be seen from the fact that the adsorption of phenosafranin, at concentrations of silver nitrate exceeding about 5×10^{-4} mole/liter, after passing through a minimum (compare Figure 12) again increases considerably, which is not the case with silver perchlorate.[62] The dis-

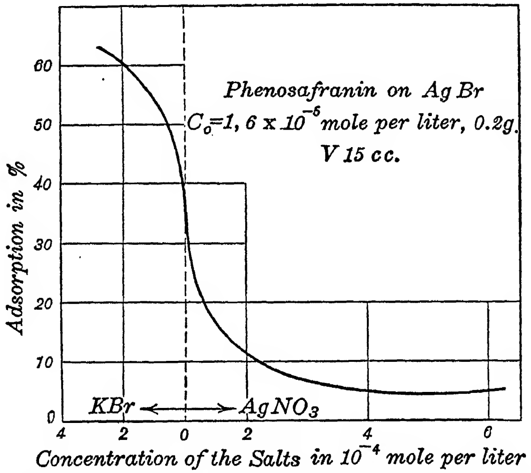

FIG. 11 Effect of KBr and $AgNO_3$ on the adsorption of phenosafranin on AgBr.

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[61] Carbonate ions also have been found to be active.

[62] The difference in the course of the two curves at concentrations below about 5 x 10^{-4} mole/liter may possibly be due to experimental error. With another preparation of silver bromide the curve for silver nitrate in the whole range was higher than for silver perchlorate (12).

placing action of silver ion therefore is partly overcome when nitrate ion is taken up. Sodium nitrate alone exerts just as little effect on the adsorption of phenosafranin as sodium perchlorate.

These peculiarities of the mechanism of the color change with phenosafranin are the reason that the change from blue to red, when titrating silver with bromide, remains sharp, not only in acid solution but also when considerable quantities of cadmium or lead ions are present (for details compare p. 246). Furthermore, since the color change is observed on the coagulated precipitate, the interfering coagulating action of multivalent ions is without effect here, in contrast to the other titrations in which a great surface development is of importance. The displacement of phenosafranin by lead ions which can be adsorbed by silver bromide (12) does not impair the color change, provided an adequate portion of the dyestuff remains adsorbed.

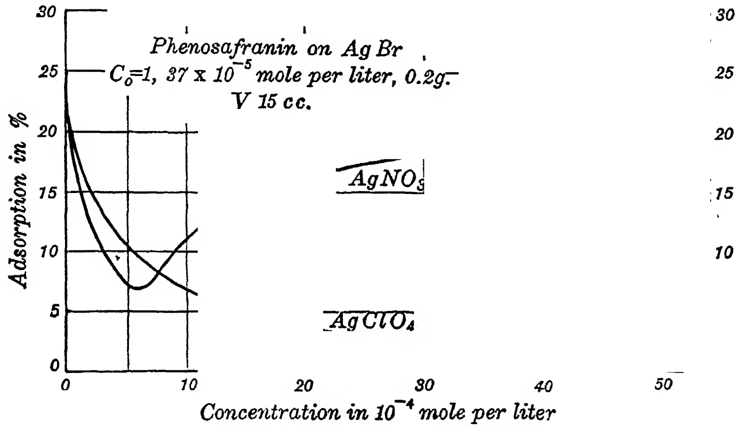

FIG. 12 Effect of $AgNO_3$ and $AgClO_4$ on the adsorption of phenosafranin on AgBr.

TITRATIONS WITH ADSORPTION INDICATORS

General Considerations. All titrations of this type have a common feature: the interface between the precipitated material and the solution plays a part in the color change. In fact, with the exception of phenosafranin (compare p. 231), the color change at the end point of the titration depends on a transfer of the dye ion, usually, from the dissolved into the adsorbed condition, in some cases (compare page 235 f.) on the reverse change of state.

In what part of the heterogeneous system is the color change observed? The consideration of this question leads to the following five cases and their respective titration precedures:

1. A considerable portion of the solid material is still in the sol form at the equivalence point, so that the color change is observed in an apparently homogeneous phase.
2. Coagulation of the sol, with simultaneous adsorption or desorption occurs exactly at the equivalence point. In this case the rôle of the dye may consist, in part, in regulating the beginning of the coagulation.
3. The sol is coagulated extensively just before the equivalence point, and not until then is the indicator transferred, with changed color, from the solution onto the precipitate or vice versa.
4. The precipitate has settled thoroughly before the end of the titration. The color change is observed in the supernatant solution, which should be as clear as possible. The color change is due to the change in concentration, that is, only to the color intensity of the indicator in the solution.
5. The color change is observed on the coagulated precipitate itself. This behavior, as yet, has been found only with phenosafranin, which in the adsorbed condition exhibits *both* transition colors. (Compare page 230 f. as well as page 245.)

Whether a given titration system corresponds to one or the other of cases 1–3 depends primarily on the concentration of the titrated solution;[63] the stability of the sol rises as the solution is made more dilute. The behavior of eosin will serve as example. (Compare page 244.)

In case 1, as the writer's own experience has shown, the point of change is easily determined and also can be established several times by titrating back and forth. Reference solutions make it possible to titrate to a given shade. Fajans and Wolff (3) did this when titrating iodide in the presence of chloride; in this case the stability of the silver iodide sol was increased by the presence of the unprecipitated chloride ion which was partly adsorbed on the silver iodide (compare page 223). Even when 0.1 *N* solutions are used, the system remains colloidal at the end point corresponding to the iodide [compare (18) (27)] unless, following Berry's example, coagulating agents are added (compare p. 224).

According to Kolthoff [(19) and (25) p. 225] the silver halides can be kept in the sol form at the end point by means of the *protective colloid,* dextrin (5 cc. of 2% chloride-free solution per 25 cc. of 0.1 *N* halide). In this way the titration may be carried out according to case 1 [(compare also Burstein (32 a)].

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[63] The influence on the coagulation point of the concentration of the dyestuff and of stirring has not been systematically studied.

Finally, it may be mentioned that the change, even after extensive coagulation, can be observed in what appears to be a *single* phase, if the sufficiently fine suspension is kept agitated by vigorous stirring. This procedure was used in most cases by Fajans and Wolff.

In case 3, both the solution and the precipitate must be watched in order to detect the end point. The color change on adsorption has to be considerable if the transition is to be striking. It may be more difficult to detect the change if part of the dye is carried down by the precipitate that has coagulated before the equivalence point has been reached, but numerous experiments, especially those of Kolthoff, have demonstrated that titrations can be carried out very accurately in case 3. This difficulty can be avoided if the dye is added only shortly before the equivalence point is reached (compare p. 242).

In case 2, the end point can be determined even without any considerable color change, provided the coagulation actually occurs reproducibly exactly at the equivalence point.

Procedure 4 can be used with particular advantage if, in the vicinity of the equivalence point, the dyestuff is strongly adsorbed on the coagulated precipitate when an excess of one of the ions is present, but easily displaced from the surface by the other ion. Then a change from colorless to colored or vice versa may be observed. Examples of this are: orthochrome T (compare p. 238), tartrazine (p. 244) or diphenylamine blue (p. 236), and also the procedure given by Berry for the titration of iodide, using rose Bengal (p. 224). The desirable clarification of the supernatant solution is promoted by adequate concentrations of the initial solutions, by addition of coagulating agents as well as by vigorous shaking.

The change with phenosafranin that occurs on the precipitate which has settled out (case 5), is very distinct: an intense color change from red to blue or vice versa.

Survey of the Methods Tested in Practice. Table I contains a number of cases that have been tested in practice; the arrangement is according to the ions being determined (column 2).[64] Where the table

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[64] References to a number of other indicators may be found in (3), (19), (25) and in the Bibliography at the end of this chapter.

TABLE I

Survey of the Practically Important Methods

1 No.	2 Titration of	3 With	4 Indicator	5 Transition	6 More Detailed Conditions	7 Literature References
1	Cl^-	Ag^+	Fluorescein	Yellow green ⇄ Pink	Solution neutral or very weakly alkaline. Cannot be used below 0.005 *N*. Compare pp. 240, 242.	Fajans and Wolff (3) Böttger and Schmitt p. 203 Kolthoff and v. Berk (17, 25)
			Dichlor (R) fluorescein	Yellow green → Red	With 0.025 *N* Cl^- up to pH ~ 4. In neutral solution down to 0.0005 *N* within 1-2%. Compare Section C, 3, α, β.	Kolthoff, Lauer and Sunde (20, 25)
			Compare Table II for other derivatives of fluorescein			
			Brilliant archil C	Red → Blue green see 11	Down to 0.005 *N* Cl^-, also in acetic acid solution and in presence of 0.5 g. $MgSO_4$.	Belladen and Piazza (27)
			Phenosafranin	Red → Blue Ppt. Ppt.	Compare Br^-. Transition less sharp than there.	Fajans and Weir (9) Berry and Durrant (28)
			Diphenylamine blue	Green → Violet Ppt. Soln.	At concentrations > 0.01 *N* Cl^- also in presence of H_2SO_4 up tc 5 *N*.	Lang and Messinger (42)
			Bromphenol blue	Yellow green → Green → Blue	Transition particularly sharp with alkaloid chlorides in acetic acid solution	Kolthoff (19)
	Br^-	Ag^+	Fluorescein	As with Chloride, adsorbed dye yellow pink		Fajans and Wolff (3)
			Eosin	Yellow red → Red violet depending on concentration	Down to 0.0005 *N* Br^-, also in acid solution at pH > 1, best in acetic acid solution. Compare pp. 222, 242, 244.	Fajans and Wolff (3) Kolthoff and van Berk (17) Kolthoff (25)
			Compare Table II for other derivatives of fluorescein			
			Chromotrope F4B	Pink → Gray with pink reflex	Down to 0.01 *N*, also in acetic acid solution, not in presence of foreign cations.	Belladen and Piazza (27)

TABLE I—(*Continued*)

1 No.	2 Titration of	3 With	4 Indicator	5 Transition	6 More Detailed Conditions	7 Literature References
			Brilliant archil C	Red → Gray green, See 11	As with Cl^-, but also in 0.02 *N* HNO_3	Belladen and Piazza (27)
			Phenosafranin	Red → Blue Ppt. Ppt. See 11	Only in presence of NO_3^- (or CO_3^{--}), also in presence of larger quantities of Zn^{++}, Cd^{++}, Pb^{++} and HNO_3.	Fajans and Weir (9) Berry and Durrant (28) Compare p. 230 f.
			Diphenylamine blue		As with chloride.	Lang and Messenger (42)
3	I^-	Ag^+	Fluorescein and derivatives, compare 2 and 4, also Table III, finally:			Fajans and Wolff (3)
			Erythrosin	Red → Red violet	Accurate only in presence of many times the equivalent quantity of foreign salts.	Rudenko (50) Compare p. 223
			Chromotrope F4B	Pink → Greenish	Down to 0.01 *N*, also in 0.01 *N* HNO_3.	Belladen and Piazza (27)
			Brilliant archil C	Violet rose → Gray green	As with Br^-.	Belladen and Piazza (27)
4	I^- in presence of Cl^-	Ag^+	Eosin, etc.	Yellow red → Red violet	Correctable over-consumption of $AgNO_3$ according to the ratio $Cl^- : I^-$.	Fajans, Hassel, Wolff (2, 3)
			Rose Bengal	Carmine red → Blue red	On addition of $(NH_4)_2CO_3$, I^- in presence of Cl^- is exact without correction.	Berry (30) Compare also p. 224 Kolthoff (18)
			Chromotrope F4B Brilliant archil C	Pink → Gray green	Transition in colloidal solution, corresponds closely to I^- alone.	Belladen and Piazza (27) Compare p. 224
5	I^- and Cl^- together	Ag^+	Bromphenol blue	Yellow → Greenish	In 0.1 *N* acetic acid solution with addition of dextrin, also in 0.01 *N* accurate within 0.5% even without dextrin.	Kolthoff (19)
			Tartrazine	Colorless → Green Soln. Soln.	Precipitation with excess Ag^+, back titration with I^-, very sharp	Compare p. 244
6	NCS^-	Ag^+	Fluorescein	As with Cl^-		Fajans and Wolff (3) Fajans and van Berk (17) Kolthoff (25)
			Eosin	As with Br^-		

TABLE I—(*Continued*)

1 No.	2 Titration of	3 With	4 Indicator	5 Transition	6 More Detailed Conditions	7 Literature References
7	$NCSe^-$	Ag^+	Fluorescein	Yellow green → Red	Down to 0.005 *N*	Ripan (46)
8	CN^-	Ag^+	Fluorescein	———	Only in presence of excess $NaHCO_3$; transition not very sharp.	Kolthoff (25, p. 248)
9	$Fe(CN)_6^{----}$	Ag^+	Fluorescein	———	———	Berry and Durrant (28)
10	$Fe(CN)_6^{----}$	Pb^{++}	Sodium alizarin sulfonate	Yellow → Rose red	Best at $\frac{N}{30}$ — $\frac{N}{60}$ $Fe(CN)_6^{----}$	Burstein (32)
11	Ag^+	Br^-	Rhodamine 6 G	Yellow red → Red violet	Down to 0.01 *N* Ag^+, particularly sharp in presence of HNO_3, up to 0.3 *N*.	Fajans and Wolff (3) Compare p. 246
		Br^-	Phenosafranin	Blue → Red Ppt. Ppt. See 2	Compare Br^- and p. 245	Fajans and Weir (9) Berry and Durrant (28)
		Br^-	Tartrazine	Yellow (colorless) → Ppt. (soln.)	At 0.1 *N* sharp also in the presence of HNO_3 up to 0.5 *N*, and Pb^{++} or Cd^{++}	Berry and Durrant (28)
		Cl^-	Tartrazine	→ Green Soln.	Compare p. 244	Berry and Durrant (28)
		NCS^-	Tartrazine	Colorless ⇄ Green Soln Soln.	0.1 *N*	Compare p. 244
		I^-	Tartrazine	As with NCS^-		
		Br^-	Brilliant archil C	Green → Pink See 2	Down to 0.005 *N* Ag^+, also with HNO_3 up to *N*/3	Belladen and Piazza (27)
12	Pb^{++}	CrO_4^{--}	Orthochrome T	Colorless ⇄ Wine Red soln. soln.	For 40 cc. neutral 0.02 *N* solution, 2 cc. 0.1% indicator soln.—accurate within 0.3%.	Fajans and Weir (9)
13	Hg_2^{++}	Cl^-	Bromphenol blue, etc.	Lilac ⇄ Yellow Ppt. Soln.	0.1 *N* solution, accuracy 0.1%	v. Zombory (61, 62)
		Br^-			0.01 *N* solution, accuracy 0.5%	Kolthoff (22)

For the following determinations the pertinent numbers of the bibliography are: CN^- with Ag^+ (58); OH^- with Pb^{++} (58); NCO^- with Ag^+ (47, 48); SO_4^{--} (49, 55, 60); NO_3^- with $TiCl_3$ (57); $C_2O_4^{--}$ with Pb^{++} (56); borate with Pb^{++} (58); PO_4^{---} with Pb^{++} (59); Ba^{++} with CrO_4^{--} (60); Pb^{++} with SO_4^{--} (49).

includes several indicators for a given titration these, as a rule, are placed in the order of increasing permissible acidity (compare colume 6). In the statement of the color changes (column 5) the direction from left to right indicates the change at the equivalence point when the precipitating ion (column 3) is added to the ion being titrated (column 2). Under these conditions, in the majority of cases, the indicator goes from the solution to the adsorbent (otherwise column 5 contains under the statement of the color, the notation Ppt., Soln.) that is, the dyestuff ion is adsorbed in the presence of an excess of the precipitating ion. From this it may be directly concluded that the dyestuff ion carries a charge of the same sign as that of the ion being determined. The conditions are reversed in the exceptional cases just mentioned. For instance, when titrating silver with tartrazine as indicator (compare No. 11) an excess of bromide causes the expulsion of the dye from the surface of the silver bromide, where it is adsorbed with a yellow color, and its passage into the solution with a deep green color. This is in harmony with the acid nature of tartrazine (a sulfonic acid).

For the special case of the basic phenosafranin (case 5 on page 234 discussed on page 230 f.) column 5 of Table I (compare under 1, 2, 11) points out correspondingly that the two transition colors are observed on the precipitate (Ppt., Ppt.); the opposite statement (Soln., Soln.) is given for the procedure 4, page 234 (compare 11, 12, for instance) where the solution alone is observed.

If column 5 contains 2 arrows, the lower one (from right to left) indicates that a titration in which the rôles of the ions given in columns 2 and 3 are exchanged also has been tested and found usable, though this has not been indicated at the appropriate place in the table. For example, it is indicated in this way only under 1 (compare also 2) but not under 11, that Ag^+ can be titrated with Cl^- (Br^-) and fluorescein as indicator. In several cases, especially when the details of the titration in the two directions are different, statements appear in both places. This is indicated by a reference: "see" to the corresponding number, instead of by the lower arrow (for example, brilliant archil C under 1 and 11).

While Table II gives the basis for a preliminary orientation as to which indicators might be suitable in a given case, more detailed information of the course of one or the other typical titrations can be derived from page 240 ff., where statements concerning the particular indicator may be found.

BEHAVIOR OF SOME INDICATORS

Fluorescein ($C_{20}H_{10}O_5Na_2$) and its Halogenated Derivatives.[66] In this class of dyestuffs, which furnished the first examples of adsorption indicators, there is a wide gradation in the deciding properties: (1) slight solubility of the silver salt of the acids concerned and the concomitant adsorbability of the dyestuff anions on the silver halides (2) the strength of these acids.[67] This is the reason for the variety of practical procedures to which these dyestuffs may be applied, as can be seen from Tables I and II. A certain disadvantage is attached to the use of these dyes because the system silver halide—dyestuff is quite *sensitive to light,* and therefore the procedure must be carried out rather rapidly and in diffused light.[68]

The applicability of the various dyestuffs of this group to the titration of the three halide ions can be learned from Table II. In it, on the basis of experiments by Pohl (7), the dyes are given in the order of the decreasing concentration at which they undergo a just perceptible color change with a fixed quantity of silver nitrate. In general, this agrees with the order of decreasing solubility of the silver salts. Therefore the following can be established as a generalization of the facts and viewpoints illustrated in Part B, where eosin and erythrosin are used as examples.

While fluorescein and those of its derivatives whose silver salts are least soluble are suitable for the titration of all three halide ions, from phloxin down the adsorbability of the dye in comparison to that of chloride ion is obviously too great to permit the titration of this ion; from di-iodo (R) fluorescein down, the same holds with reference to bromide ion, so that the remaining [69] dyes of the Table are suitable for the titration of

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[65] Details concerning the use as adsorption indicator of the following 6 dyes can be found on page 240ff; the appropriate page is indicated by the number in the parentheses: Uranin A conc. (242); dichlor (R) fluorescein sodium salt (243); eosin G conc. (244); tartrazine (244); phenosafranin (245); rhodamine 6 G as chloride or nitrate (245). Compare also Table I.

[66] (P) or (R) indicates whether the substitution is in the phthalic acid or in the resorcin residue.

[67] When the substitution is in the resorcin residue, the insolubility of the silver salts and the adsorbability of the dye anion increases, in general, with rising halogen content and with increasing atomic weight of the halogen. Substitution in the phthalic acid residue has rather the opposite effect. Compare Table II.

[68] Fajans and Hassel (1) in experiments directed toward the closer study of the known photochemical sensitization of silver bromide by these dyes encountered the behavior which is the basis of the new method.

[69] Compare Table I, number 3 regarding erythrosin.

iodide only.[70] The adsorbability of thiocyanate ion is close to that of bromide (compare page 213); consequently thiocyanate can be titrated with fluorescein as well as with eosin. The applicability of the other dyes to the titration of thiocyanate has not been studied as yet.

The facts given in Table I, namely that fluorescein can be used only at pH > 7, dichlor (R) fluorescein at pH > 4, eosin at pH > 1,[71] are, of course, closely connected with the resulting increase of the dissociation constants of the dye acids on the introduction of the halogen. The stronger the dye acid the less at a given pH, will the formation of undissociated acid interfere with the adsorption of the dye anion. It may be worth noting that the adsorbability and the strength of the acid, in general, rise in the same sequence (Table II). Their strong acid nature explains why the two sulfonic acids, brilliant archil C and tartrazine, may be used for the titration of silver with bromide (compare Table I, number 11) even in the presence of 0.3 or 0.5 *N* nitric acid.

TABLE II

SUITABILITY OF DERIVATIVES OF FLUORESCEIN AS INDICATORS

		Cl^-	Br^-	
	Solubility of Silver Salt Mole/Liter	1×10^{-5}	5×10^{-7}	1×10^{-8}
Fluorescein (fl.)	(10^{-4})	+ +	+ +	+ +
Dimethyl (R) fl.		+ +	+	+
Dichlor (P) fl.		+	+	+
Dichlor (R) fl.		+ +	+ +	+ +
Tetrachlor (P) tetrabrom (R) fl. (Phloxin)			+	+
Dibrom (R) fl.			+ +	+
Dichlor (P) tetrabrom (R) fl.			+	+
Tetrabrom (R) fl. (Eosin)	5×10^{-5}		+ +	+ +
Di-iodo (R) fl.				+ +
Dimethyl (R) di-iodo (R) fl.				+ +
Dichlor (P) tetra-iodo (R) fl. (Rose Bengal)	1×10^{-6}			+ +
Tetra-iodo (R) fl. (Erythrosin)*				

* Compare Table I, No. 3.

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[70] By this is meant the titration of alkali halide in neutral solution and in the absence of foreign salts. The effect of the latter and of acid reaction can be learned, in part, from Table I and has been studied in detail, particularly by Rudenko (50).

[71] Iodide was titrated in strong acetic acid solution also with rose Bengal as indicator, compare (50).

In Table II the meaning of the symbols is: + the dye [dibrom (R) fluorescein for instance], gives a usable change in the titration of the particular halide (I^-) with Ag^+; ++ the titration (for Br^-) has been studied in some detail; — that (for Cl^-) no usable change has been found. The solubilities of the silver salts have been taken from the compilation of Fajans and Erdey-Grúz (4). The figure for silver fluoresceinate is from Kieser, Dissertation Freiburg i. Br. 1904.

Fluorescein. Indicator solution 0.2%, either of the sodium salt (uranin) in water, or of the acid in alcohol. Table I and the bibliography show that fluorescein may be used in numerous titrations. The following are mentioned to supplement the special conditions given in Table I.

Fajans and Wolff (3) added the indicator (1.5–6 drops per milli-mole of halide) to the halide solution to be titrated and then introduced the 0.1 *N* silver nitrate solution with stirring. Their aim was to observe the transition in that part of the sol which had not yet been precipitated. For this the most favorable concentration range of the halide solution was 0.05–0.01 *N*. At higher concentrations, the sol coagulates too soon and too extensively to permit the use of procedure 1 (compare page 234).

Kolthoff and van Berk (17), when using 0.1 *N* chloride solution, treated it with a slight deficit of 0.1 *N* silver nitrate solution, and like Böttger and Schmitt (page 203) only then added the indicator (1–2 drops per milli-mole of halide) and then, with vigorous shaking, finished the titration with 0.01 *N* silver nitrate solution. The coagulated precipitate is colored pink by the adsorbed dye exactly at the equivalence point. This procedure corresponds most closely to case 3, page 234.

If, as is usually the case, the dye is added before mixing the solutions, the beginning of the coagulation depends on the concentration of the halide, as described under eosin (p. 244). This indicator however, can be used in the titration of bromide, thiocyanate, and iodide down to lower concentrations than can fluorescein in the chloride titration.

In this last case, the change is indistinct below 0.01 *N* and an over-consumption of silver nitrate is encountered. The titration curve of fluorescein, which is more weakly adsorbed than eosin, may correspond to the type of Curve C, Figure 4, and be less steep than it. Since the strong fluorescence of the dissolved fluorescein is weakened only slightly by a small quantity of the sol, the adsorption must be considerable to produce a color change, and this can be expected only with a marked excess of silver.

At concentrations above 0.01 *N*, however, a definite transition color and the correct equivalence point may be reproduced easily within 0.1–0.2% in parallel titrations.[72]

Because of the colloidal chemical and photochemical instability of the systems, comparison solutions cannot be kept available. The inexperienced therefore, will find it advisable not to allow too much time to elapse between standardizing the solutions and carrying out the titrations, so that a given shade may always be reached.

Dichlor (R) Fluorescein. $C_{20}H_8Cl_2O_5Na_2$. 0.1% solution of the sodium salt in water, or of the acid in 60–70% alcohol. This indicator, whose properties lie between those of fluorescein and eosin, was introduced by Kolthoff, Lauer and Sunde (20). It is particularly suitable in titrations of chloride in weakly acid and very dilute solutions (see Table II). 0.025 *N* chloride solution is recommended particularly; 2 drops of indicator are used for each 10 cc.; with very dilute solutions, not more than 2–4 drops should be added for each 50 cc. In these solutions the end point is reached when the color changes distinctly to orange; pink and red shades appear only with excess of silver ion.

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[72] With reference to the position of the point of change when iodide is titrated in the presence of fluorescein, the over-consumption of 0.6% given by Fajans and Wolff (3) as compared with the equivalence point determined with dimethyl (R) di-iodo (R) fluorescein and by the Volhard method which give concordant results, could not be confirmed. Kolthoff and van Berk (10) found the position of the change point to be the same with fluorescein, eosin and di-iodo (R) fluorescein, and when the titration was carried to a distinct or dark coloration of the silver iodide the result agreed with the Volhard figure or entailed an excess consumption of about 0.2%. Rudenko (50) found that titrations using fluorescein and eosin agreed with those carried out by the Volhard procedure. A re-examination in the writer's laboratory showed that fluorescein, dichlor (R) fluorescein, brilliant archil C, chromotrope F4B agree with the Volhard results within 0.1%. With eosin and dimethyl (R) di-iodo (R) fluorescein there is consumed 0.3% less silver nitrate than in the Volhard method if the titration is carried to the first distinct color change, and the deficit is even less when the final color is still more pronounced. The small discrepancies between the results of the various workers are surely due, in part, to their choice of different shades as representing the end point.

Contamination of commercial preparations of iodide with chloride can lead also to somewhat divergent results with different indicators because, with fluorescein, for instance, the sum of the iodide and chloride is involved, while with eosin the change occurs when the iodide alone has been consumed (compare Table I, numbers 4 and 5). Studies with Portillo (14) of the best commercial preparations of potassium iodide which, however, were distinctly contaminated with chloride, yielded the following results. 50 cc. of 0.1 *N* potassium iodide diluted to 350 cc., on titration gave the first change with eosin when about 0.2 cc. less 0.1 *N* silver nitrate was added than was necessary to produce clarification without eosin. The end point of the transition interval with eosin that coincided with the coagulation practically agreed, however, with the clear point without eosin.

Eosin. $C_{20}H_6Br_4O_5Na_2$. 0.5% solution. Fajans and Wolff (3) thought that the main advantage of this indicator, which is suitable for the titration of bromide, iodide and thiocyanate, is the fact that it can be used in acid solution. Kolthoff and van Berk (17) however, emphasized also the sharpness of its color change, particularly in acetic acid solution, and showed that it can be used over a wide range of concentrations (0.1–0.0005 *N* halide). For this reason, the phenomena accompanying the use of eosin will be described in some detail and these will apply *ceteris paribus* to several other indicators at various concentrations. Compare especially [(17) p. 382 ff. and (25) p. 225 ff.] the sources of the following statements and references.

The coagulation occurs before the equivalence point is reached, if 0.1 *N* solutions of halide and silver nitrate are used. Compare page 234, case 3. For instance, silver chloride coagulates 1% before the equivalence point if fluorescein is used and 0.5% before, if dichlor (R) fluorescein serves as indicator. In the titration of bromide in the presence of eosin (2 drops of indicator per 25 cc.) the silver bromide flocculated 0.05% before the equivalence point as determined potentiometrically. Exactly at this point the precipitate became pale red and 0.05% excess of silver ion made it brick red.

If 0.01 *N* solutions are used (1 drop of indicator per 25 cc. of potassium bromide solution) "during the titration the liquid remains pink; just before the end point the color becomes more blue, at the end point, the silver bromide suddenly flocculates and is then decidedly red." This corresponds to case 2, page 234.

Case 1 is clearly exemplified if solutions still more dilute are used. This holds particularly for the demonstration experiment described on page 205, in which the colloid at the equivalence point was 0.0003 *N*. "In the titration of 0.001 *N* solutions, coagulation could be detected no longer, the color changes suddenly from pink to purple red. We could still titrate 100 cc. of 0.0005 *N* KBr solution to within 1%."

Tartrazine. $C_{15}H_9N_4O(SO_3Na)_2COONa$. 0.5% solution. This indicator was recommended by Berry and Durrant (28) and although it involves a color anion, in the case of chloride and bromide a distinct change is obtained only when silver is titrated with the halide. If 0.1 *N* solutions are employed the silver halide coagulates well in the presence of the dye which, if used in the quantity given below, is adsorbed extensively with yellow color in the presence of excess silver ion. Displaced from the surface by an excess of halide ion it turns the almost colorless solution greenish.

If silver is titrated (Berry and Durrant used the sulfate in the presence of equal quantities of Cd^{++}) to a rich green, the consumption of bromide is 0.1% less than if the titration is carried to the equivalence point as determined by the clear point; at a pale green the divergence is 0.25%. The titration curve, therefore, would seem to approximate type a of Figure 6. Four drops of indicator solution are used for each 100 cc. of 0.1 *N* potassium bromide solution.

Kolthoff's statement (25) that the change is not reversible and that consequently the titration must be made very cautiously was confirmed by the writer for chloride and bromide. However, it was shown that for thiocyanate and iodide (cases which Berry and Durrant did not study) the change in both directions is very sharp and reversible. With an excess of silver ion, silver thiocyanate takes on a flesh color. Tartrazine proved excellently suited also for the determination of the sum of iodide and chloride. The mixture is shaken vigorously (to cause coagulation) while silver nitrate is added in slight excess, and the back-titration with iodide continued until the clear and colorless solution becomes distinctly green. 2 drops of indicator solution are used in the titration of 20 cc. of the single 0.1 *N* solutions, 3 drops for 40 cc. of the mixture of potassium iodide and potassium chloride.

Phenosafranin, $C_{18}H_{15}N_4Cl$. 0.2% solution. As was noted in Table II and explained in more detail on page 230 f., in the titration of bromide with silver nitrate both colors of the very well marked and excellently reversible transition (with excess of silver ion, from red to blue) are observed on the settled precipitate (compare page 234, procedure 5); therefore, the procedure should not be carried out in solutions that are too dilute.[73] Weir (9) used 0.05 *N*, Berry and Durrant (28) 0.1 *N* solutions. The change is equally sharp in either direction. Studies with Van Artsdalen, which were conducted somewhat more accurately than the earlier ones with Weir, have shown that after precipitation of 50 cc. of 0.05 *N* solutions, a color change of red to blue or vice versa at the equivalence point, as determined nephelometrically, requires quantities of 0.01 *N* silver nitrate or potassium bromide that are less than 0.1 cc., that is, less than 0.04% of the quantities titrated. A distinct color change on part of the grains of the precipitate can be brought about by the addition of still smaller quantities of the solutions. About 0.06–0.1 cc. of the indicator solution is used per milli-mole of silver bromide.[74]

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[73] The intensity of the red color of the solution does not alter noticeably at the transition. Compare page 232.

Berry and Durrant, when titrating silver-cadmium mixtures, added an excess of bromide and titrated back to blue with silver nitrate. In 3 trials, the consumption of bromide was 0.12 ± 0.09% less than that when the clarification point was determined.

The red color of aqueous phenosafranin solution is gradually shifted to blue violet by nitric acid. If, at the end of the titration the concentration of the acid is below 0.2 *N*, the position of the change was unaltered even though the transition was not so sharp. With a final concentration of 0.3 *N*, the dye was added only toward the end of the titration, otherwise the point of change is shifted in the direction of greater bromide consumption. Berry (29) states that sulfuric acid interferes; it bleaches the blue color of the precipitate.

Phenosafranin is a suitable indicator in the rapid determination of silver, even in alloys high in lead (9). A mixture of 30 cc. of 0.01 *N* silver nitrate and 30 cc. of 0.9 *M* lead nitrate (the relative weights of silver and lead were 1:170) when titrated in neutral solution with bromide gave a result for silver within +0.9%

Phenosafranin behaves toward chloride as it does toward bromide. However the change is not quite so sharp as with bromide. According to Weir, the analogous changes are still less sharp when mercurous nitrate is titrated with potassium bromide and even worse with potassium chloride and phenosafranin as indicator.

Rhodamine 6 G, $(C_{26}H_{27}O_3N_2)^+$ as chloride or nitrate. Wolff and the writer (3) found this dye quite suitable for the titration of silver with bromide in nitric acid solution. These observations [compare also (25)] were confirmed recently with Van Artsdalen. The chloride permits the preparation of 0.1% solution, but only 0.05% water solution of the less soluble nitrate is possible.

The transition (yellow pink → red violet) is observed in the whole solution, even though the sol is partially coagulated (compare Section C, 1). Therefore, the silver solution to be titrated should not be too concentrated, best 0.02–0.01 N. The change is sharper in not too strong (up to about 0.3 *N*) nitric acid than in neutral solution. About 0.3 cc. of the 0.05% nitrate solution of the indicator is used per milli-mole of silver bromide.

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[74] For very accurate determinations, it would be more rational to use the nitrate rather than the chloride of the dyestuff.

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